Understanding titanium-catalysed radical-radical reactions: A DFT study unravels the complex kinetics of ketone-nitrile couplings

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General Remarks

The Turbomole 6.5 and Orca 3.03 program packages were used for the calculations.[1,2] COSMO*therm* was used for the calculation of solvation energies. To speed up calculations, the RI-J approximation was used to treat the coulomb exchange in the DFT calculations,[3] as well as the RI-C approximation for the correlation energies in the double hybrid functionals and the MP2 and CCSD(T) calculations.[4] The D3 dispersion correction with Becke-Johnson damping (D3BJ) was applied in all DFT calculations.[5,6]

In detail, **Turbomole** was used for all structure optimizations, frequency analyses, and single point calculations, as well as CCSD(T) reference calculations. Turbomole was NOT used for the calculation of the broken-symmetry (BS) transition states.
Orca was used for the calculation of the broken-symmetry (BS) transition states, which included the structure-optimizations, frequency analyses and single-point calculations of the BS-transition states and the C-C coupling precursors.

All structure optimizations were finalized using the TPSS functional[7] together with the def2-TZVP basis set[8] and matching auxiliary basis sets.[9] The conductor-like screening model (COSMO) [10] was switched on for the optimizations. Thus, the final level for optimizations was: RI-TPSS-D3BJ-COSMO/def2-TZVP.

Frequency analyses were carried out numerically using the *NumForce* script as implemented in Turbomole or by using the *NumFreq* option of Orca. Stationary points (minimum structures) were characterized by the absence of imaginary frequencies. Transition states showed a single imaginary frequency that matched the transition vector. The correction to the Gibbs Free Energy was obtained using *freeh* as implemented in Turbomole (unscaled), or from the Orca-output ($=G–E_{el}$).

Single-point calculations with the BP86,[11] TPSS,[7] PBE0,[12] B3LYP,[13] PW6B95,[14] B2PLYP[15,16] functionals were carried out with Turbomole using the def2-QZVP basis set and matching auxiliary basis sets.[17] All single-point calculations with the DSD-PBEP86 functional[18] were performed with Orca and using the def2-QZVPP basis set together with matching auxiliary basis sets.[8,9,17]

Free Energies of Solvation were calculated using the COSMO-RS solvation model as implemented in COSMO*therm*.[19,20] We therefore used COSMO files generated from RI-BP86/def-TZVP[21] single point calculations.

CCSD(T) reference energies[22] for the benchmark calculations were computed with Turbomole on the triple-ζ level and extrapolated to the quadruple-ζ level using additional MP2 calculations.[23] The following basis sets with matching auxiliary c-basis sets were employed on the triple-ζ level (denoted AwCVTZ): H,C,N,O: aug-cc-pVTZ; Cl: aug-cc-pV(T+d)Z; Ti, Zn: aug-cc-pwCVTZ. The following basis sets with matching auxiliary c-basis sets were employed on the quadruple-ζ level (denoted AwCVQZ): H,C,N,O: aug-cc-pVQZ; Cl: aug-cc-pV(Q+d)Z; Ti, Zn: aug-cc-pwCVQZ.[24]
The aug-cc-pwCVQZ c-basis sets for Ti, Zn were generated using *cbasopt* as implemented in Turbomole.
See the corresponding chapters below for details.

Visualization. All rendered pictures of the transition states in the manuscript were generated using *CYLview*.[25] Additional representations of molecular structures in this supporting information were generated with *Avogadro*.[26]

Turbomole settings and parameters:

- A relative permittivity of $\varepsilon_r = 7.4$ was used for all COSMO calculations.
- All structure optimizations were carried out using the TPSS functional with COSMO switched on. All optimizations were finalized on the RI-TPSS-D3BJ-COSMO/def2-TZVP level using tight convergence criteria:

  control file: scfconv 8, grid m4, weight derivatives
  jobex start parameters: -ri -energy 7 -gcart 4

- Frequency analyses were carried out using the program *NumForce*. *NumForce* calculations were started with the options -ri -central -cosmo. The vibrational frequencies were used unscaled (factor = 1.0000).
- Single point calculations were carried out using the setting $scfconv 6.
- For MP2 and CCSD(T) calculations the automatically defined frozen core was appropriate for most structures. The settings for some titanium(III) complexes had to be adjusted manually to fit the basis sets. The following settings for frozen core orbitals were applied: C, N, O: 1; Si, Cl, Ti, Zn: 5. The (U)HF reference wavefunctions were converged using the parameters $scfconv 8, $denconv 0.10000000E-06
- B2PLYP calculations were carried out with the $marij option switched on.

Orca settings and parameters:

- All optimizations were carried out using the *Grid 3 FinalGrid5* option with COSMO(THF) switched on
- Frequency calculations were carried out using the option *NumFreq*
- For all single point calculations the *Grid4 FinalGrid5* setting and the *RIJCOSX* approximation with suitable auxiliary j-bases were applied.
- DSD-PBEP86 calculations were carried out using the input parameters given on the *ORCA input library* webpage.[27]
- The same frozen cores were applied for MP2 calculations as for Turbomole calculations. Usually the setting *Ewin* in combination with *Emin = -6.000* was sufficient to give correct frozen core orbitals.
- Broken Symmetry calculations (including numerical frequency calculations) were carried out using the *BrokenSym 1,1* option.

A note on the structure optimization of $ZnCl_3(THF)^-$

The structure of $ZnCl_3(THF)^-$ converged using the TPSS-D3BJ-COSMO/def2-SVP method, but attempted optimization using the def2-TZVP basis set failed due to oscillation (even using $scfconv 9, grid 6 and smaller step size). A calculation of the hessian at this point and on the def2-SVP optimized geometry resulted in zero imaginary frequencies. To fulfill the tight structure optimization criteria, the optimization was completed with ORCA (Grid 3, FinalGrid5, TightSCF, TightOpt), resulting in the optimized minimum structure (showing no imaginary frequency).

Benchmark Calculations

The reactions shown in eqs 1.1–1.6 in the manuscript were used to evaluate the BP86, TPSS, PBE0, B3LYP, PW6B95, B2PLYP and DSD-PBEP86 functionals. As reference served CCSD(T) values that were extrapolated to the quadruple-ζ level using the following scheme:

$$E_{\mathrm{CCSD(T)/AwCVQZ}} \approx E_{\mathrm{CCSD(T)/AwCVTZ}} + E_{\mathrm{MP2/AwCVQZ}} - E_{\mathrm{MP2/AwCVTZ}}$$

AwCVTZ refers to Cl: aug-cc-pV(T+d)Z; Ti, Zn: aug-cc-pwCVTZ; all other: aug-cc-pVTZ
AwCVQZ refers to Cl: aug-cc-pV(Q+d)Z; Ti, Zn: aug-cc-pwCVQZ; all other: aug-cc-pVQZ

No auxiliary aug-cc-pwCVQZ c-basis sets were available to us for Ti and Zn. We therefore generated corresponding cbases using the Turbomole program *cbasopt* (see Appendix B).

The mean absolute deviation from the CCSD(T)-value was calculated from the values obtained for each functional over all six test reactions (n=6):

$$MAD = \frac{1}{n}\sum_{i=1}^{n}\left|E^{DFT}{}_i - E^{CCSD(T)}{}_i\right|$$

Table S1 lists the results of the benchmark calculations. The electronic energies and coordinates for the species involved are listed in Appendix A.

Table S1. Energies for the test reactions in kcal mol^{-1}.

Reaction	BP86	TPSS	PBE0	B3LYP	PW6B95	B2PLYP	DSD-PBEP86	CCSD(T)/AwCVQZ
1.1	–24.4	–23.6	–19.6	–19.6	–17.9	–18.0	–15.7	**–16.9**
1.2	130.2	129.4	125.5	126.4	124.5	125.9	124.0	**126.3**
1.3	38.1	38.2	36.6	37.2	38.2	38.2	38.9	**38.7**
1.4	–1.4	–2.1	–2.5	–1.3	–1.7	–1.1	–0.9	**–0.8**
1.5	–69.8	–67.8	–70.2	–66.1	–66.6	–71.3	–72.9	**–70.8**
1.6	41.9	33.4	19.7	28.9	22.8	32.2	25.8	**22.0**
MAD	5.6	4.3	1.4	2.7	1.5	2.2	1.6	-
MAX Deviation	20.0	11.4	2.7	7.0	4.2	10.3	3.8	-

Optimization of aug-cc-pwCVQZ *c-basis* sets for Ti and Zn

The *c-bases* for Ti and Zn were optimized on the atoms using the program *cbasopt* and MP2/aug-cc-pwCVQZ calculations as reference. For the Ti c-basis set, convergence was not achieved after 5000 iterations using tight criteria. However, the accuracy was more than sufficient for our calculations. The optimization of the cbasis set for Zn converged using tight criteria.

Table S2. Results of test MP2/aug-cc-pwCVQZ calculations with the new c-basis sets.

Compound	E_{corr}(MP2) / Hartree	E_{corr}(RI-MP2) / Hartree	$\frac{E_{corr}(MP2) - E_{corr}(RI-MP2)}{E_{corr}(MP2)} \times 100$	ΔE_{corr} / kJ mol^{-1}
Ti	–0.4494919855	–0.4494965138	–0.001007%	0.0118891343
TiF_3	–1.3024534355	–1.3024433427	0.000775%	–0.0264987071
Zn	–1.0749503153	–1.0749517052	–0.000129%	0.0036492106
ZnF_2	–1.6502963407	–1.6502935097	0.000172%	–0.0074328669
ZnF_3^-	–1.9580803488	–1.9580736665	0.000341%	–0.0175443133

Ti [16s15p13d13f11g8h6i4k]
Output from job.last:

```
     Statistics delta(I)/Hartree:
     ...
     5000    0.00000130589459

      ***************************************************************
                          CONVERGENCE INFORMATION

                               Converged?     Value      Criterion
             Energy change          yes      0.0000000   0.0000010
             MAX basis grad.        yes      0.0000004   0.0010000
      ***************************************************************
```

Output from *cbasopt*:

```
  cycle = 5000    delta      =      0.0000013059
   scalnorm = 0.000000e+00    expnorm = 0.112552e-04    contnorm = 0.000000e+00
total basis set gradient is now: 1.12552e-05  (log:          5)
```

Zn [16s15p13d13f11g8h6i4k]
Output from job.last:

```
Statistics delta(I)/Hartree:
     ...
     5000    0.00000644105843

      ***************************************************************
                          CONVERGENCE INFORMATION

                               Converged?     Value      Criterion
             Energy change          yes      0.0000000   0.0000010
             MAX basis grad.        yes      0.0000006   0.0010000
      ***************************************************************
```

Output from *cbasopt*:

```
  cycle = 5000    delta      =      0.0000064411
   scalnorm = 0.000000e+00    expnorm = 0.429489e-05    contnorm = 0.000000e+00
total basis set gradient is now: 4.29489e-06  (log:          5)
```

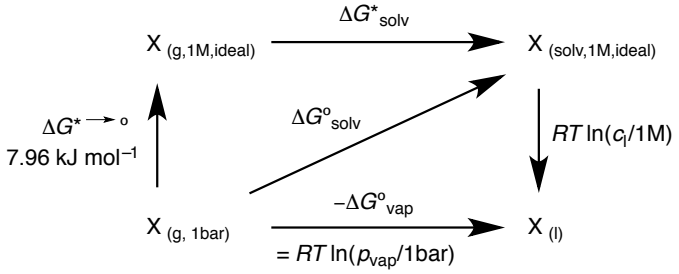
Gibbs Free Energy of Phase-Transitions

Born-Haber Cycle and Interconversion Corrections

The solvation energy calculated by common quantum chemical solvation models is based on equal concentrations in gas phase and solution.[28] This usually corresponds to the transfer from a one-molar ideal gas (24.79 bar at 298.15 K) to a one-molar ideal solution, denoted in this work as ΔG^*_{solv} (Scheme S1).[29] The *Gibbs* standard solvation energy (ΔG^o_{solv}), however, refers to the transfer from an ideal gas at 1 bar to a one-molar ideal solution. ΔG^o_{solv} can be calculated from ΔG^*_{solv} by addition of the chemical potential difference between an ideal gas at 1 mol L^{-1} and at 1 bar (= 7.96 kJ mol^{-1} or 1.90 kcal mol^{-1}):

$$\Delta G^o_{solv} = \Delta G^*_{solv} + RT\ln(24.79)$$
$$= \Delta G^*_{solv} + \mathbf{7.96\ kJ\ mol^{-1}}$$

For gas-to-liquid transfers, the concentration of the solute in itself has to be considered in addition, requiring for an additional correction by $RT\ln(c_l/1M)$. The result is the negative free energy of vaporization ($-\Delta G^o_{vap}$). In the case of gas-to-solid transfers, the free energy of sublimation has to be calculated.



Scheme S1. Interconversion Scheme for the calculation of solvation energies for a compound X.

In the following, the required interconversion corrections for $Zn_{(g,\ 1bar)} \rightarrow Zn_{(s)}$ and $THF_{(g,\ 1bar)} \rightarrow THF_{(l)}$ are described in detail:

Quasi-experimental free sublimation energy of zinc at 298.15 K and thermodynamic correction

To estimate the Gibbs free energy for the reduction of Ti^{IV} to Ti^{III} by zinc powder, the Gibbs free sublimation energy of zinc at 298.15 K had to be calculated. This was achieved by calculation of the standard free vaporization energy ΔG^o_{vap} from the vapor pressure $p_{vap}^{298.15}$, which was obtained from the Antoine equation and literature values for the Antoine constants A and B as described:[30]

$log_{10}(p_{vap}) = A + B \cdot T^{-1}$

A = 6.102 (see Ref. 30; the value is for the calculation of p in atm)

B = –6776 (see Ref. 30; the value is for the calculation of p in atm))

T = 298.15 K

$\Longrightarrow\ p_{vap} = 2.372 \cdot 10^{-17}$ atm
$= 2.404 \cdot 10^{-17}$ bar

$\mathbf{-\Delta G^o_{vap} = RT\ln p_{vap} = -94.86\ kJ}$ (= –22.67 kcal)

For confirmation, this value was calculated from the standard free energy of formation of zinc in the gas and solid phases using the thermochemical data for zinc metal as provided in the NIST Webbook:[31]

$\Delta H^o_{f(g)}$ = 130.42 kJ mol^{-1} $S^o_{(g)}$= 160.99 J mol^{-1} K^{-1}
$S^o_{(s)}$= 41.72 J mol^{-1} K^{-1}

$\Delta G^o_{vap} = \Delta H^o_{f(g)} - T\Delta S_{(g-s)}$
ΔG^o_{vap} = 94.86 kJ
$\mathbf{\Delta G^o_{subl} = -\Delta G^o_{vap} = -94.86\ kJ}$

Zinc: Correction to free energy at 298.15 K

For a monoatomic ideal gas, only the translational entropy is relevant. Hence, the following can be applied:

$U^\circ = 3/2RT$

$H^\circ = U^\circ + pV = U^\circ + RT = 5/2\ RT = 6.20$ kJ mol^{-1}

$S^\circ_{(g,\ 1\ bar)} = 160.990$ J mol^{-1} K^{-1} (see NIST Webbook)

$\Delta G^\circ_{corr} = H^\circ - TS^\circ$

$= \mathbf{-41.8\ kJ\ mol^{-1}}$ (= –10.0 kcal mol^{-1})

This was the thermal correction to the free energy, which was added to the electronic energy in order to obtain $G^\circ_{(g,\ 1\ bar)}$(Zn).

Solvation energy of THF in THF and in the THF-BnCN mixture

We briefly confirmed the accuracy of the COSMO-RS solvation energy of THF by comparison of the calculated value with a quasi-experimental solvation energy of THF in THF (= $-\Delta G^\circ_{vap}$).

The free vaporization energy of THF was calculated using the Antoine equation and literature values for the Antoine constants A, B and C obtained from the NIST webbook:[32]

$log_{10}\ (p_{vap}) = A - [B\cdot(T+C)^{-1}]$

A = 4.12118

B = 1202.942

C = –46.818

T = 298.15 K

$\Longrightarrow\ p_{vap} = 0.216$ bar

$-\Delta G^\circ_{vap} = RT \ln p_{vap} = -3.80$ kJ (= –0.91 kcal)

The calculated energy for the solvation of THF in THF (including the correction 1 bar → 12.34 M) was found to be:

ΔG°_{solv}(COSMO-RS) = –0.91 kcal mol^{-1}

This was in excellent agreement with the quasi-experimental value.

For the THF-BnCN (0.71:0.29, mole fraction) solvent mixture, the solvation energy was found to be:

ΔG°_{solv}(COSMO-RS) = –1.05 kcal mol^{-1}

This value was expected to be of similar accuracy. It further showed that the presence of BnCN as co-solvent had only little influence. This was also observed for the THF/THF-BnCN solvation energies of all other species, which differed by ≤ 1 kcal mol^{-1}.

A Note on Conformer Searches

In order to determine the lowest energy conformer, we calculated several reasonable conformers (by hand) for each molecule. A molecular dynamics conformer search with simulated annealing was not applied, since it would have to be carried out at least a double-zeta DFT-level to give reasonable energies for the titanocene-containing structures. The conformer search results for compound **10** are given as representative example. The lowest energy conformer was used for the transition state search. A similar procedure was applied to all other compounds and transition states. For triethylamine and triethylammonium ($HNEt_3^+$) it was found that the minimum conformer was in agreement with the experimental structure of triethylamine in solution.[33]

10-anti:

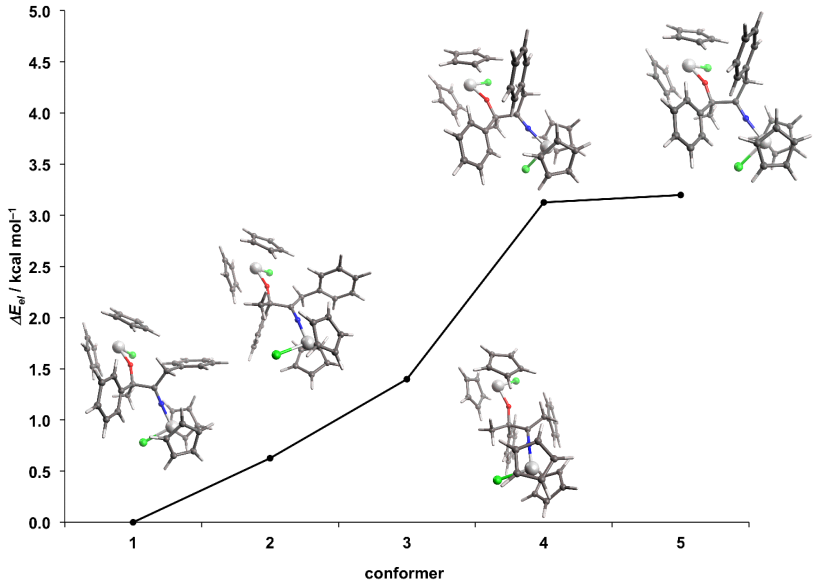


Figure S1. Conformer search for **10-anti**.

10-syn:

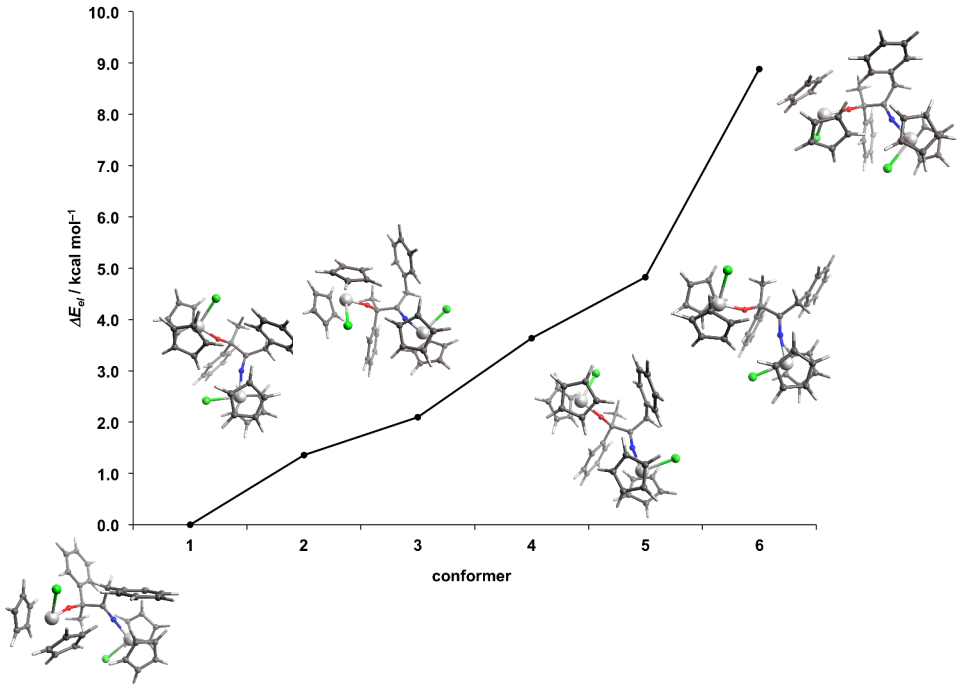


Figure S2. Conformer search for **10-syn**.

The minimum conformer of **10-anti** was found to be overall lowest conformer and therefore selected to represent compound **10**. The minimum conformers of **10-anti** and **10-syn** were used for the transition state searches for **TS-10-anti** and **TS-10-syn**.

Localization of the C-C Coupling Transition States

The C-C coupling transition states were localized by first carrying out a relaxed scan on the broken-symmetry hypersurface. As starting point, we used the lowest energy conformers of the corresponding C-C coupling products. Afterwards, the highest-lying structure was used as a starting point for the transition state optimization. We found it most practical to first carry out the optimization using the smaller def2-SVP basis set followed by a frequency analysis. Then, the mode for the C-C bond formation was identified. The resulting Hessian was than used for the final optimization along the transition state mode using the def2-TZVP basis set. Example input file for **TS-10-anti**:

```
! RI UHF TPSS def2-TZVP def2-TZVP/J OptTS Grid3 FinalGrid5 D3BJ TIGHTSCF NumFreq xyzfile
! COSMO(THF)
%geom
inhess Read
InHessName "TS_def2svp.hess"
Trust 0.3
MaxIter 1000
TS_Mode {B 4 5}   # This mode corresponded to the C-C bond to be formed
end
end
%scf
BrokenSym 1,1
MaxIter 1000
end
%pal
nprocs 24
end
* xyzfile 0 1 coord.xyz
...
```

Spin-projection techniques were not applied,[34] since these were previously discussed to degrade the quality of potential energy surfaces in DFT calculations.[35]

In the following, the results of the relaxed scans will be shown for the broken-symmetry transition states. The reference energy is the combined energy of the C-C coupling precursors if not noted otherwise.

Transition State TS-10-anti

Figure S3 shows the broken-symmetry relaxed scan on the TPSS-D3BJ-COSMO/def2-TZVP level. In order to illustrate the effect of the broken-symmetry formalism, the singlet and triplet energies for the points of the relaxed broken-symmetry scan have been calculated as well. Figure S4 shows the same scan together with the spin contamination (it should approach $<S^2> = 1$ upon homolytic dissociation of the C-C bond).

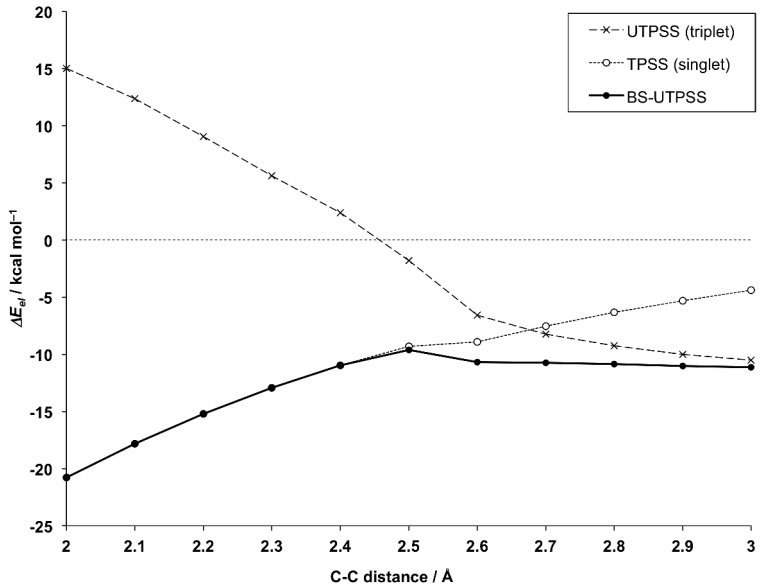


Figure S3. Relaxed broken-symmetry scan for **TS-10-anti** together with the singlet and triplet energies of each point.

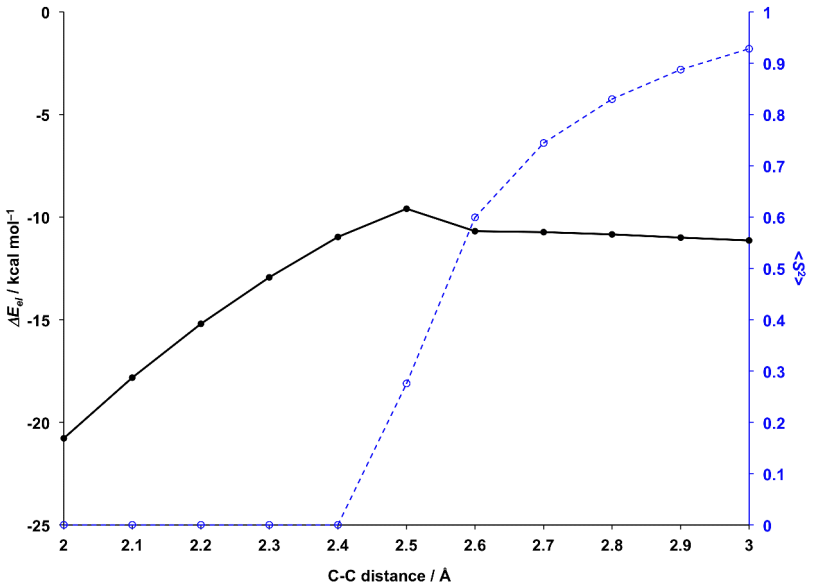


Figure S4. Relaxed broken-symmetry scan for **TS-10-anti** together with the spin contamination (TPSS-D3BJ-COSMO/def2-TZVP).

Transition State TS-10-syn

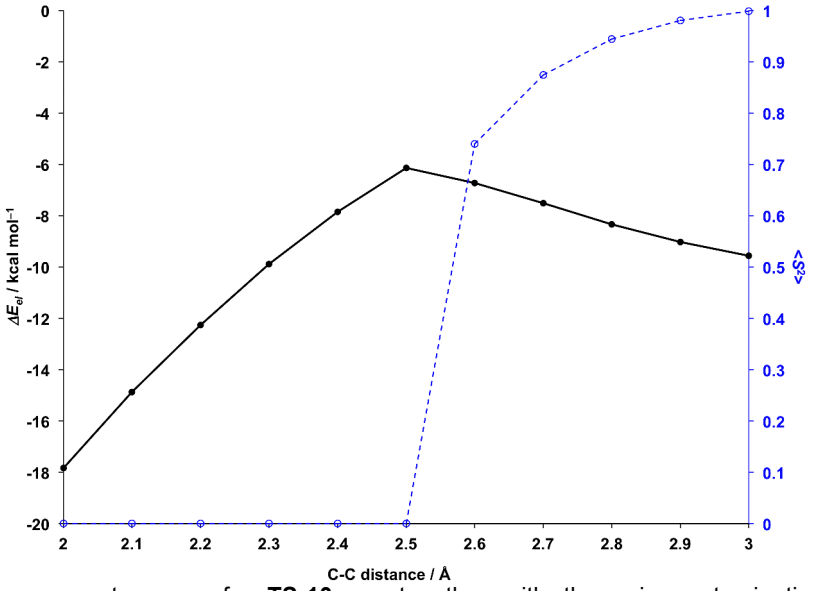


Figure S5. Relaxed broken-symmetry scan for **TS-10-syn** together with the spin contamination (TPSS-D3BJ-COSMO/def2-TZVP).

Transition State TS-26

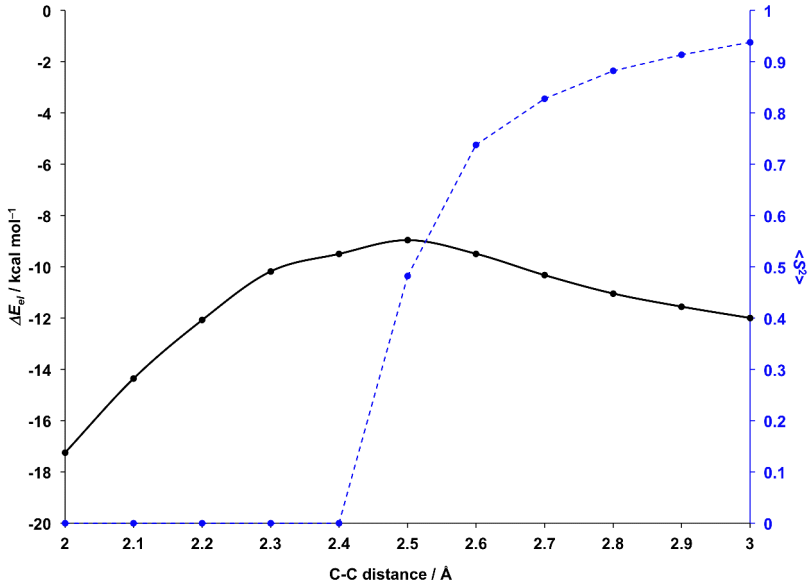


Figure S6. Relaxed broken-symmetry scan for **TS-26** together with the spin contamination (TPSS-D3BJ-COSMO/def2-TZVP).

Transition State TS-27

Here, the relaxed scan was performed on the TPSS-D3BJ-COSMO/def2-TZVP level.

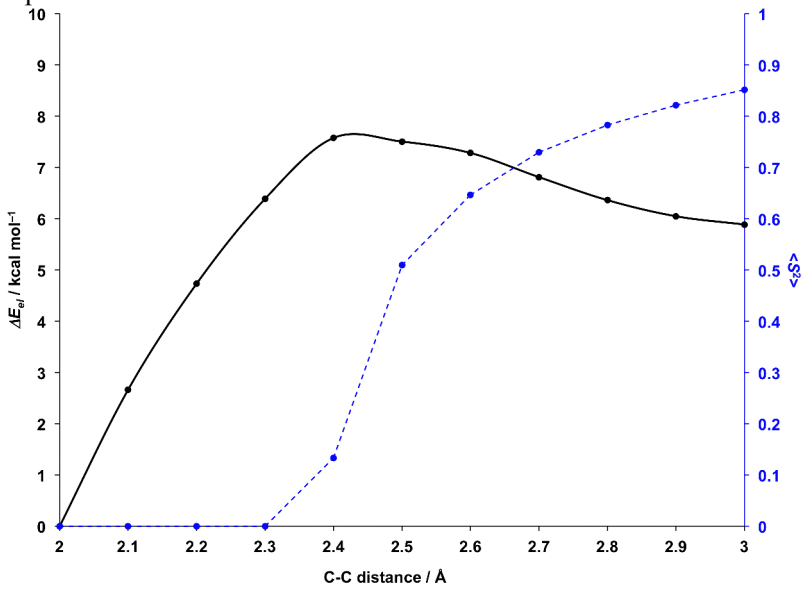


Figure S7. Relaxed broken-symmetry scan for **TS-27** together with the spin contamination. TPSS-D3BJ-COSMO/def2-SVP, energies in relation to C-C distance = 2 Å.

Transition State TS-28

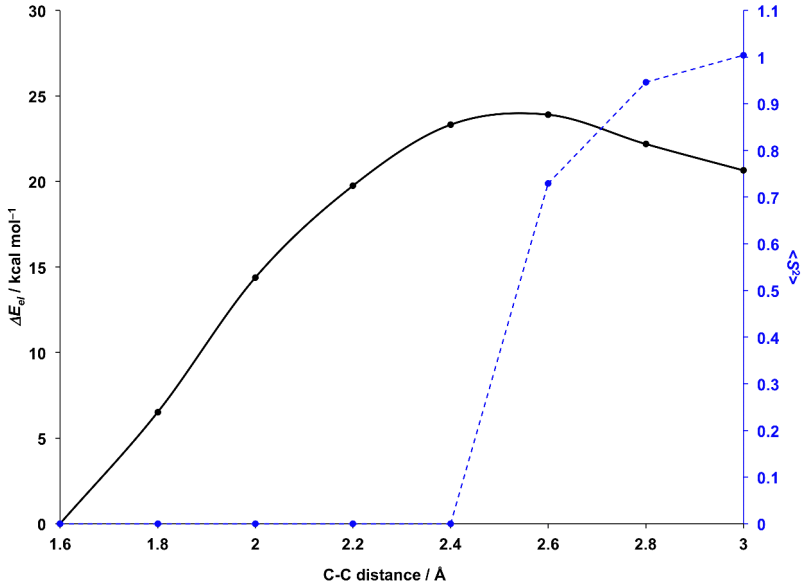


Figure S8. Relaxed broken-symmetry scan for **TS-28** together with the spin contamination. TPSS-D3BJ-COSMO/def2-SVP, energies in relation to C-C distance = 1.6 Å.

Alternative mechanism via an aggregate of 8 and 9

Radical-radical cross-couplings often proceed through the formation of an aggregate, which is then followed by a unimolecular radical coupling. Such a mechanism was previously proposed for related titanium(III)-catalysed pinacol-pincol couplings, for example.[36] However, the titanium(III) centres of complexes 8 and 9 have only four available coordination sites that are already occupied by two η^5-coordinated Cp ligands, the substrate (ketone or nitrile) and a chloride. Formation of a chloride-bridged aggregate would lead to pentacoordinated titanium(III) centres that cannot be formed and that do not present minima on the hypersurface. The formation of the cationic aggregate **23**, on the other hand, is possible and leads to a feasible unimolecular coupling pathway as depicted in Scheme 6.

This is supported by preliminary attempts to model a chloride-bridged aggregate of 8 and 9. The optimization of such an aggregate on the RI-TPSS-D3(BJ)-COSMO/def2-SVP level led to the extrusion of a chloride anion and the formation of **23** with a chloride remaining coordinated to the C-H bonds of the Cp ligands (Figure S9). This corresponds to the formation of **23**, which in returns supports the reaction of 23 to complex 28.

Along these lines, a corresponding bistitanated product complex with two bridging chlorides does not represent a valid minimum either. Here, loss of the η^5-coordination of one Cp-ligand occurs at each titanium center in order to allow the additional Ti-Cl bond to form (Figure S10).

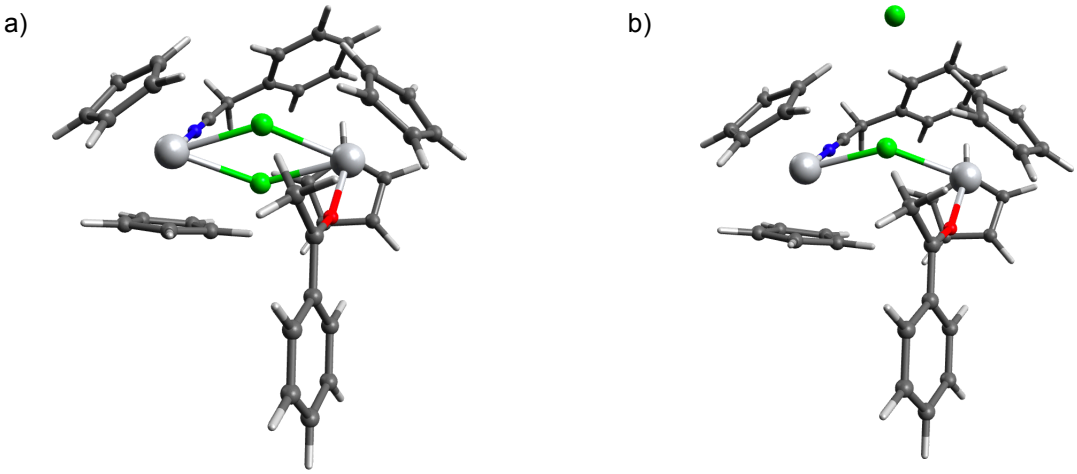


Figure S9. Attempted optimizations of a chloride bridged neutral substrate complex. a) Input structure, b) result.

a) b)

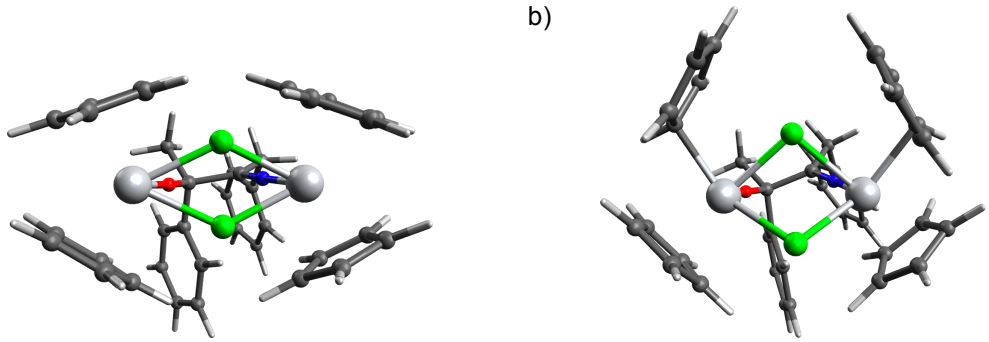


Figure S10. Attempted optimizations of a chloride bridged neutral product complex. a) Input structure, b) result.

Energy profile including B2PLYP and DSD-PBEP86 energies

Off-cycle intermediates were omitted for clarity. As discussed in the manuscript, no transition states were calculated using the double-hybrid functionals.

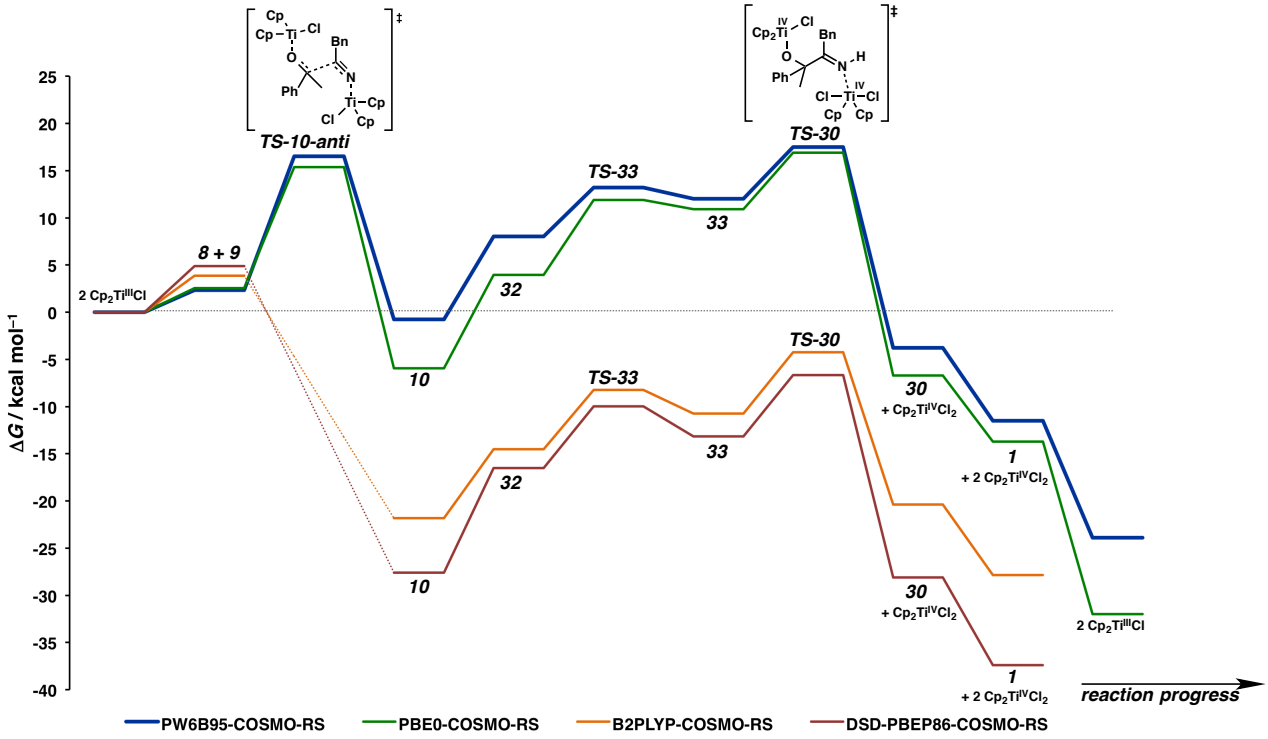


Figure S11. Hypersurface for the neutral reaction pathway including the B2PLYP and DSD-PBEP86 energies. Off-cycle intermediates and transition states are omitted. For the B2PLYP and DSD-PBEP86 profiles, only the stoichiometric reaction is shown.

Experimental Details

Kinetic Profile of the Reaction with $(EtCp)_2TiCl_2$ and Cp_2TiCl_2

The catalytic reductive coupling of acetophenone with benzyl cyanide showed an increasingly significant initiation time at higher loadings of $(EtCp)_2TiCl_2$ or with Cp_2TiCl_2 as catalyst (Figure S12). A more detailed analysis of the kinetics will be reported in due course. The curves shown in the following were recorded using a ReactIR in situ IR spectrometer in analogy to our earlier measurements.[37]

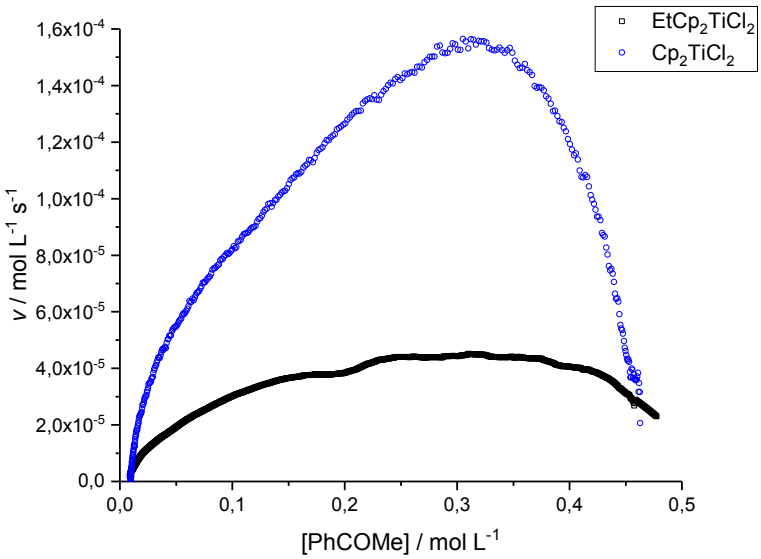


Figure S12. Kinetic profiles of the reaction with $(EtCp)_2TiCl_2$ (10 mol%, black) and with Cp_2TiCl_2 (10 mol%, blue) as catalyst.

Determination of the Free Energy of Activation with Cp_2TiCl_2 as Catalyst

The rate constants for the reaction profile — after the inition time was reached — were then determined at 35 ºC, 30 ºC, 25 ºC, 20 ºC, and 15 ºC by plotting the graphical rate equation followed by linear regress analysis (Figure S13). Using an oil (or water) bath is recommended for temperature control and reproducibility. We further confirmed that the experiments and kinetic traces were reproducible and each experiment was run two times and the average curve was used for the analysis. The analyses were carried out using *OriginPro*.[38] For the graphical rate equation, an order of 1.7 in Cp_2TiCl_2, an order of 0.6 in PhCOMe, and an order of –1 in BnCN were identified by different excess experiments as optimal parameters. Here, the order in BnCN was different from the order reported in presence of $(EtCp)_2TiCl_2$ as catalyst (–3).[37] A detailed investigation of the order in nitrile is ongoing and the results will be reported in due course.

From an Eyring-Plot (Figure S14) the following data was obtained:

$$\Delta H^{\ddagger,298.15} = 8.0 \text{ kcal mol}^{-1}$$
$$\Delta S^{\ddagger,298.15} = -36.7 \text{ cal mol}^{-1} \text{ K}^{-1}$$
$$\Delta G^{\ddagger,298.15} = 18.9 \text{ kcal mol}^{-1}$$

For comparison, we also carried out a determination of the Gibbs Free Activation Energy assuming an overall 0th order behavior at the fastest point of the reaction. This was done by using v_{max} obtained from plots of v vs t as well as by a direct linear regression of plots of c vs t after the initiation time. Both returned values of $\Delta G^{\ddagger,298.15}$ = 19.9 kcal mol^{-1}, which deviated from the value returned from the graphical rate equation analysis by 1 kcal mol^{-1}. Considering the complex catalytic system, the heterogeneous reaction mixture, and the differential nature of the rate determination from IR kinetics, this 1 kcal mol^{-1} difference might still be within the error of the measurement.

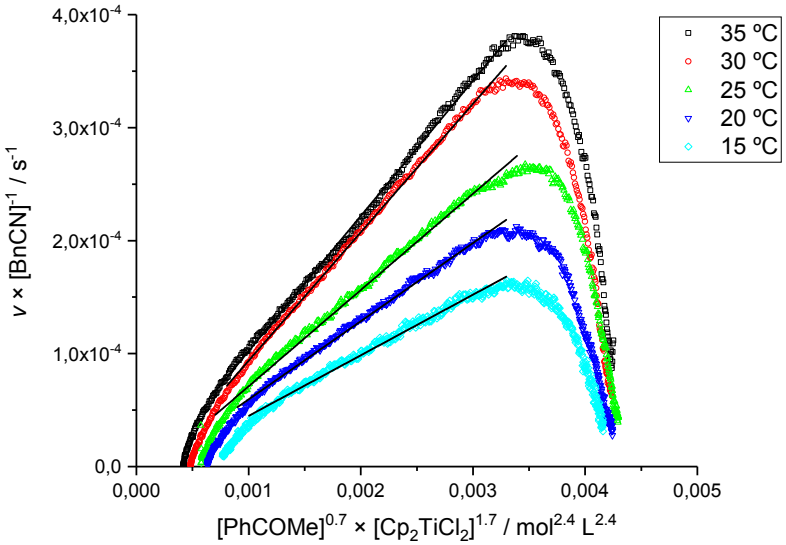


Figure S13. Determination of *k* using the graphical rate equation.

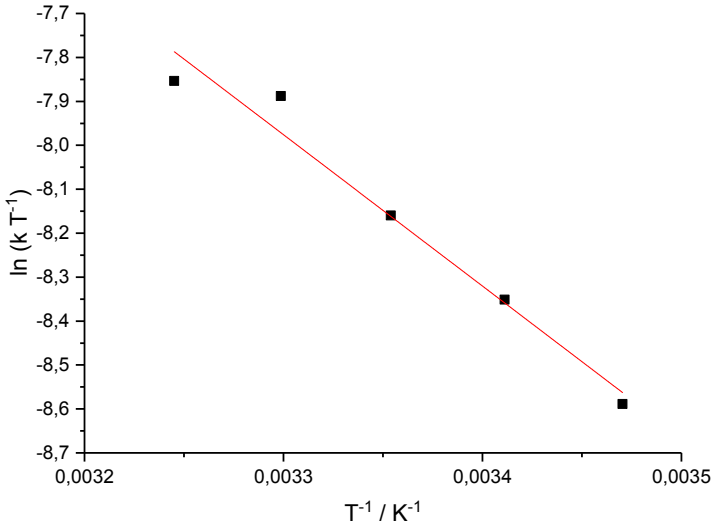


Figure S14. Eyring-Plot.

Solubility of Et_3N•HCl in absence and in presence of $ZnCl_2$

A 10 mL vial containing a magnetic stir bar was charged with 822 mg Et_3N•HCl (5.97 mmol) and weighted. THF (3 mL) was added and the mixture was stirred for 1.5 h. The solution was carefully pipetted off and the vial was weighted again to obtain the residual mass of Et_3N•HCl. The process was repeated and from the average mass balance the amount of dissolved Et_3N•HCl was calculated. The experiment was repeated with 409 mg $ZnCl_2$ (3.00 mmol) being added showing a rapid solution of an equimolar amount.

Without $ZnCl_2$: Δm = 11.7±0.7 mg
c = 2.82±0.0016×10^{-2} mol L^{-1}

With 0.5 eq. $ZnCl_2$: Δm = 455.9 mg (= 55%) ; more than 50% Et_3N•HCl were dissolved
c' = 1.1 mol L^{-1} ; c' = corresponding concentration of Et_3N•HCl

Appendix A — Tables and Coordinates for the Benchmark Calculations

Table S3. Electronic single point energies for the compounds of the benchmark calculations in Hartree.

Compound	applied symmetry	BP86 def2-QZVP	TPSS def2-QZVP	PBE0 def2-QZVP	B3LYP def2-QZVP	PW6B95 def2-QZVP	B2PLYP def2-QZVP	DSD-PBEP86 def2-QZVPP	CCSD(T) AwCVQZ
HCN	C_{6v} (C_{2v})[a]	–93.473784	–93.482866	–93.351220	–93.419944	–93.582209	–93.404952	–93.313460	–93.3061975529
DME	C_{2v}	–155.113271	–155.128825	–154.916989	–155.017815	–155.280260	–154.982602	–154.841459	–154.8351611139
NH_3	C_{3v} (C_1)[a]	–56.596113	–56.594570	–56.520666	–56.558279	–56.652072	–56.546029	–56.495655	–56.4976261650
$NH_4(DME)^+$	C_s	–212.086484	–212.103938	–211.816890	–211.953246	–212.308424	–211.904357	–211.714062	–211.7078694679
NH_4Cl	C_{3v} (C_1)[a]	–517.486459	–517.450036	–517.202872	–517.342427	–517.838382	–517.253019	–517.015342	–516.8609160269
$ZnCl_2$•$(DME)_2$	C_{2v}	–3010.671522	–3010.370711	–3009.346136	–3009.933848	–3012.236190	–3009.607956	–3008.617172	–3008.2216966782
$ZnCl_3(DME)^-$	C_s	–3315.962994	–3315.609025	–3314.625582	–3315.214671	–3317.659573	–3314.849800	–3313.812678	–3313.2679458812
$ZnCl_3(NH_3)^-$	C_1	–3217.447997	–3217.078161	–3216.233174	–3216.757138	–3219.034031	–3216.414996	–3215.468301	–3214.9316102138
Me_2TiCl	C_s	–1389.808578	–1389.696732	–1389.154297	–1389.448009	–1390.591814	–1389.251006	–1388.733772	–1388.4541223480
$Me_2Ti(DME)^+$	C_s	–1084.347868	–1084.289809	–1083.706871	–1083.999603	–1085.000922	–1083.841403	–1083.370552	–1083.2394489148
$Me_2Ti(Cl)(HCN)$	C_s	–1483.321246	–1483.217162	–1482.536764	–1482.899164	–1484.202538	–1482.684679	–1482.072247	–1481.7872444989
$Me_2Ti(HCN)^+$	C_s	–1022.709041	–1022.643830	–1022.140304	–1022.399059	–1023.300479	–1022.259660	–1021.837608	–1021.7044998335
$TiH_3(HCN)$	C_1	–944.816469	–944.740018	–944.342406	–944.555330	–945.307948	–944.432601	–944.090964	–943.9701442432
$TiH_3(CH_2O)$	C_s	–965.945096	–965.866861	–965.444340	–965.667315	–966.439041	–965.542594	–965.184403	–965.0619025075
$H_3TiN{=}CHCH_2OTiH_3$	C_s	–1910.872711	–1910.714846	–1909.898638	–1910.327907	–1911.853158	–1910.088793	–1909.391499	–1909.1448689505
Zn	C_1	–1779.720124	–1779.444665	–1779.185956	–1779.376582	–1780.343922	–1779.260930	–1778.916964	–1778.8541355229
Me_2TiCl_2	C_{2v}	–1850.204411	–1850.057502	–1849.333101	–1849.731865	–1851.275840	–1849.467587	–1848.762934	–1848.3202341107

[a] For CCSD(T) calculations, the symmetry shown in brackets was applied.

Table S4. T_1 and D_1 diagnostics for the coupled-cluster calculations on the CCSD(T)/AwCVTZ-level.

Compound	Norm(t1)	N (corr. e^-)	T_1 diagnostic	D_1 diagnostic (CCSD)
HCN	0.04518	10	0.0143	0.0283
DME	0.04622	20	0.0103	0.0263
NH_3	0.02383	8	0.0084	0.0186
$NH_4(DME)^+$	0.04910	28	0.0093	0.0263
NH_4Cl	0.03167	16	0.0079	0.0230
$ZnCl_2$•$(DME)_2$	0.09972	74	0.0116	0.0480
$ZnCl_3(DME)^-$	0.08879	62	0.0113	0.0449
$ZnCl_3(NH_3)^-$	0.07684	50	0.0109	0.0410
Me_2TiCl	0.20065	33	0.0349	0.0956
$Me_2Ti(DME)^+$	0.20152	45	0.0300	0.1229
$Me_2Ti(Cl)(HCN)$	0.24856	43	0.0379	0.1317
$Me_2Ti(HCN)^+$	0.21489	35	0.0363	0.1214
$TiH_3(HCN)$	0.24349	25	0.0487	0.1150
$TiH_3(CH_2O)$	0.30012	27	**0.0578**	**0.2166**
$H_3TiN{=}CHCH_2OTiH_3$	0.23270	52	0.0323	0.0989
Zn	0.07878	20	0.0176	0.0618
Me_2TiCl_2	0.14418	40	0.0228	0.0750

A note on the T_1-diagnostic: The open-shell T_1 diagnostic defined by Jayatilaka and Lee[39] could not be determined by us in a straightforward fashion using the Turbomole output. We therefore used the following definition in all cases (N = number of correlated electrons):[40]

$$T_1 = \frac{\|t_1\|}{\sqrt{N}}$$

In a recently published work by Jiang, Yonker and Wilson,[41] new thresholds of $T_1 < 0.05$ and $D_1 < 0.15$ were suggested for 3d transition-metal-containing molecules to still signal a reliable single-reference calculation. With exception of $TiH_3(CH_2O)$, all diagnostics were within these limits.
For comparison, we performed a CCSD(T)/aug-cc-pVTZ calculation for $TiH_3(CH_2O)$ using a frozen core of 11 orbitals with the Gaussian 09 program package.[42] Here, the T_1-diagnostic for open-shell systems is implemented and a value of $T_1 = 0.0375$ was returned, which is in good agreement with the thresholds above. One reason for the observed behavior could be partial location of the unparied electron at the titanium and the carbon center (the distribution may vary depending on the method).

Output excerpt of the Turbomole UHF/AwCVTZ calculation of the titanium(III)-formaldehyde complex $TiH_3(CH_2O)$:

```
atomic populations from spin  density:
atom          sum       n(s)       n(p)       n(d)       n(f)       n(g)
  1 o          0.02344  -0.00013   0.02298   0.00030   0.00029   0.00000
  2 ti         0.23689   0.00258   0.01866   0.21459   0.00093   0.00015
  3 c          0.86201   0.04345   0.80376   0.01593  -0.00113   0.00000
  4 h         -0.03600  -0.03573  -0.00030   0.00004   0.00000   0.00000
  5 h         -0.03630  -0.03603  -0.00032   0.00004   0.00000   0.00000
  6 h         -0.01334  -0.01337   0.00003  -0.00001   0.00000   0.00000
  7 h         -0.01835  -0.01949   0.00114  -0.00000   0.00000   0.00000
  8 h         -0.01835  -0.01949   0.00114  -0.00000   0.00000   0.00000
```

Coordinates

Energies (RI-TPSS-D3-COSMO/def2-TZVP) are reported in Hartree. The symmetry that was applied is reported and the lowest energy orbital occupation is reported for titanium(III)-complexes. All structures were found to be stationary points (numerical frequency calculations returned no imaginary frequencies).

HCN

```
3
Energy = -93.48507642040
N     0.0000000    0.0000000   -1.1277320
C     0.0000000    0.0000000    0.0269776
H     0.0000000    0.0000000    1.1007543
Symmetry: c6v
Symmetry for ccsd(t): c2v
```

dme

```
9
Energy = -155.1210455519
C     0.0000000   -1.1786828    0.0390092
O     0.0000000    0.0000000    0.8445829
H    -0.8948658   -1.2178854   -0.6001675
H     0.0000000   -2.0320791    0.7205314
H     0.8948658   -1.2178854   -0.6001675
C     0.0000000    1.1786828    0.0390092
H    -0.8948658    1.2178854   -0.6001675
H     0.8948658    1.2178854   -0.6001675
H     0.0000000    2.0320791    0.7205314
$symmetry c2v
```

NH_3

```
4
Energy = -56.59462591500
N     0.0000000    0.0000000   -0.2978972
H    -0.4702325    0.8144666    0.0992528
H    -0.4702325   -0.8144666    0.0992528
H     0.9404650    0.0000000    0.0992528
$symmetry c3v
$symmetry for ccsd(t): cs
```

$[NH_4(dme)]^+$

```
14
Energy = -212.1731615623
N    -2.1803606    0.2495884    0.0000000
O     0.4276713   -0.4306623    0.0000000
C     1.1780929   -0.1373009    1.1958261
H     2.0852368   -0.7508500    1.2210512
H     0.5364257   -0.3890504    2.0417752
H     1.4478053    0.9253988    1.2269270
C     1.1780929   -0.1373009   -1.1958261
H     1.4478053    0.9253988   -1.2269270
H     0.5364257   -0.3890504   -2.0417752
H     2.0852368   -0.7508500   -1.2210512
H    -1.1384861    0.0123330    0.0000000
H    -2.6303619   -0.1440067   -0.8299346
H    -2.3188873    1.2625987    0.0000000
H    -2.6303619   -0.1440067    0.8299346
$symmetry cs
```

NH_4Cl

```
6
Energy = -517.4731180582
N     0.0000000    0.0000000   -0.5054667
Cl    0.0000000    0.0000000    2.4779212
H     0.0000000    0.0000000    0.5862298
H     0.4803383   -0.8319704   -0.8530605
H     0.4803383    0.8319704   -0.8530605
H    -0.9606767    0.0000000   -0.8530605
$symmetry c3v
$symmetry for ccsd(t): c1
```

$ZnCl_2(dme)_2$

```
21
Energy = -3010.294394873
Zn     0.0000000     0.0000000     1.7726575
Cl     0.0000000    -2.0412520     2.6040626
Cl     0.0000000     2.0412520     2.6040626
O      1.5525333     0.0000000     0.3629601
O     -1.5525333     0.0000000     0.3629601
C      1.8842896     1.2024584    -0.3696840
H      1.3126137     1.2389555    -1.3038469
H      2.9571679     1.2034643    -0.5846330
H      1.6218433     2.0411003     0.2745629
C      1.8842896    -1.2024584    -0.3696840
H      2.9571679    -1.2034643    -0.5846330
H      1.3126137    -1.2389555    -1.3038469
H      1.6218433    -2.0411003     0.2745629
C     -1.8842896    -1.2024584    -0.3696840
H     -1.3126137    -1.2389555    -1.3038469
H     -2.9571679    -1.2034643    -0.5846330
H     -1.6218433    -2.0411003     0.2745629
C     -1.8842896     1.2024584    -0.3696840
H     -1.6218433     2.0411003     0.2745629
H     -2.9571679     1.2034643    -0.5846330
H     -1.3126137     1.2389555    -1.3038469
$symmetry c2v
```

$[ZnCl_3(dme)]^-$

```
13
Energy = -3315.583270821
Zn    -1.5819701     0.9985763     0.0000000
Cl    -2.6379618     0.5157186    -1.9340775
Cl    -0.2952842     2.8610670     0.0000000
Cl    -2.6379618     0.5157186     1.9340775
O     -0.0336098    -0.4963943     0.0000000
C      0.7774411    -0.5117050    -1.1961234
C      0.7774411    -0.5117050     1.1961234
H      0.0842286    -0.5003531     2.0373454
H      1.4224020     0.3738869     1.2217848
H      1.3828427    -1.4245497     1.2053905
H      0.0842286    -0.5003531    -2.0373454
H      1.3828427    -1.4245497    -1.2053905
H      1.4224020     0.3738869    -1.2217848
$symmetry cs
```

$[ZnCl_3(NH_3)]^-$

```
8
Energy = -3217.068562580
Zn    -0.0007989     0.0003651     0.1042554
Cl     0.5005410     2.1640746    -0.4272478
Cl    -2.1250149    -0.6470569    -0.4271425
Cl     1.6238889    -1.5153347    -0.4226627
N     -0.0000059    -0.0002315     2.2035088
H     -0.6848194    -0.6591348     2.5730388
H     -0.2272095     0.9221976     2.5738847
H      0.9134187    -0.2648794     2.5713447
$symmetry c1 (c3 or c3v led to a transition state)
```

Me_2TiCl

```
10
Energy = -1389.664124723
Ti    -0.4019647     0.7277734     0.0000000
Cl    -2.5010030     1.5595533     0.0000000
C      0.2505061    -0.1841757     1.7529160
H      1.0151070     0.5064348     2.1526511
H      0.7231267    -1.1525645     1.5401091
H     -0.5372368    -0.3133712     2.5046487
C      0.2505061    -0.1841757    -1.7529160
H      0.7231267    -1.1525645    -1.5401091
H      1.0151070     0.5064348    -2.1526511
H     -0.5372368    -0.3133712    -2.5046487
$symmetry cs
```

```
$alpha shells
 a'      1-20                                   ( 1 )
 a"      1-9                                    ( 1 )
$beta shells
 a'      1-19                                   ( 1 )
 a"      1-9                                    ( 1 )
```

[$Me_2Ti(dme)]^+$

```
18
Energy = -1084.332147863
C    -1.8269547   -0.0691405    1.5569647
Ti   -0.8198291   -1.0008573    0.0000000
H    -1.6758302    1.0172491    1.5815498
H    -1.3674117   -0.5170046    2.4567298
H    -2.9017503   -0.2908288    1.5636303
C    -1.8269547   -0.0691405   -1.5569647
H    -1.6758302    1.0172491   -1.5815498
H    -2.9017503   -0.2908288   -1.5636303
H    -1.3674117   -0.5170046   -2.4567298
O     1.0593825   -0.3133074    0.0000000
C     1.7884725    0.0491886   -1.2204316
H     1.1971148   -0.3145019   -2.0600273
H     2.7637727   -0.4396769   -1.1883365
H     1.8854945    1.1356022   -1.2560637
C     1.7884725    0.0491886    1.2204316
H     2.7637727   -0.4396769    1.1883365
H     1.1971148   -0.3145019    2.0600273
H     1.8854945    1.1356022    1.2560637
$symmetry cs
$alpha shells
 a'      1-20                                   ( 1 )
 a"      1-13                                   ( 1 )
$beta shells
 a'      1-20                                   ( 1 )
 a"      1-12                                   ( 1 )
```

$Me_2TiCl(HCN)$

```
13
Energy = -1483.184737767
Ti   -0.2251138   -0.6132420    0.0000000
C    -0.8856125    0.2971552    1.7672126
H    -1.8977743   -0.0604418    2.0101181
H    -0.9301672    1.3820369    1.5821306
H    -0.2277533    0.1075447    2.6271488
C    -0.8856125    0.2971552   -1.7672126
H    -1.8977743   -0.0604418   -2.0101181
H    -0.2277533    0.1075447   -2.6271488
H    -0.9301672    1.3820369   -1.5821306
Cl   -0.5724155   -2.8866906    0.0000000
N     1.7746333   -0.1777229    0.0000000
C     2.9184717    0.0312969    0.0000000
H     3.9802185    0.1881917    0.0000000
$symmetry cs
$alpha shells
 a'      1-26                                   ( 1 )
 a"      1-10                                   ( 1 )
$beta shells
 a'      1-25                                   ( 1 )
 a"      1-10                                   ( 1 )
```

$[Me_2Ti(HCN)]^+$

```
12
Energy = -1022.693836282
Ti   -0.1168062    0.9002030    0.0000000
C    -0.9229742    0.0941693    1.7091506
H    -1.6917600    0.8159295    2.0343783
H    -0.1939301   -0.0538157    2.5148662
H    -1.4021065   -0.8598040    1.4502127
C    -0.9229742    0.0941693   -1.7091506
H    -1.6917600    0.8159295   -2.0343783
H    -1.4021065   -0.8598040   -1.4502127
```

```
H    -0.1939301   -0.0538157   -2.5148662
N     1.8040547    0.1304752    0.0000000
C     2.8735803   -0.3031408    0.0000000
H     3.8676964   -0.7152624    0.0000000
$symmetry cs
$alpha shells
 a'      1-19                                   ( 1 )
 a"      1-8                                    ( 1 )
$beta shells
 a'      1-18                                   ( 1 )
 a"      1-8                                    ( 1 )
```

$TiH_3(HCN)$

```
7
Energy = -944.7329597332
N     0.4492268   -0.7427200    0.0610184
Ti   -0.7090843    0.9473411   -0.0871688
C     1.1134621   -1.6889979    0.1440811
H    -2.4027718    0.5142239   -0.2140518
H    -0.2079540    1.8110956    1.3466939
H     1.7329211   -2.5630189    0.2202870
H     0.0242001    1.7220762   -1.4708598
$symmetry c1
```

$TiH_3(CH_2O)$

```
8
Energy = -965.8479250018
O     0.1856256   -0.3824940    0.0000000
Ti   -0.5046950    1.2694372    0.0000000
C     0.6223622   -1.6098293    0.0000000
H     1.6969888   -1.7714907    0.0000000
H    -0.1060264   -2.4162464    0.0000000
H    -2.2167743    1.0170506    0.0000000
H     0.1612595    1.9467863    1.4429381
H     0.1612595    1.9467863   -1.4429381
$symmetry cs
$alpha shells
 a'      1-16                                   ( 1 )
 a"      1-5                                    ( 1 )
$beta shells
 a'      1-16                                   ( 1 )
 a"      1-4                                    ( 1 )
```

$H_3TiN{=}CHCH_2OTiH_3$

```
15
Energy = -1910.678092718
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Ti   -2.7762356    2.2030498    0.0000000
C    -0.6657413   -0.0585516    0.0000000
C     0.8107339    0.2876281    0.0000000
O     1.6036111   -0.8770926    0.0000000
H     1.0440492    0.8825116    0.8910387
H     1.0440492    0.8825116   -0.8910387
Ti    2.5175576   -2.3530908    0.0000000
H    -0.9096245   -1.1315317    0.0000000
H     4.1512484   -1.8151021    0.0000000
H     1.9946218   -3.1243095   -1.4453404
H     1.9946218   -3.1243095    1.4453404
H    -3.6853337    2.1054352   -1.4653249
H    -1.7019429    3.5475589    0.0000000
H    -3.6853337    2.1054352    1.4653249
$symmetry cs
```

Zn

```
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Me_2TiCl_2

```
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C      0.0000000    1.6275712    0.4346846
H      0.9009777    1.5839174    1.0605082
H     -0.9009777    1.5839174    1.0605082
H      0.0000000    2.5461231   -0.1654842
C      0.0000000   -1.6275712    0.4346846
H      0.9009777   -1.5839174    1.0605082
H      0.0000000   -2.5461231   -0.1654842
H     -0.9009777   -1.5839174    1.0605082
Cl     1.8969584    0.0000000   -1.9656955
Cl    -1.8969584    0.0000000   -1.9656955
$symmetry c2v
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Appendix B — aug-cc-pwCVQZ c-bases for Ti and Zn

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$cbas
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```

Appendix C — Tables for the Compounds in the Manuscript

Table S5. Relative Gibbs Free Energies in solution of all titanium species (Turbomole).

Identifier	Compound / Short Name	$\Delta G_{THF\text{-}BnCN}$ / kcal mol^{-1}			
		PW6B95-COSMO-RS	PBE0-COSMO-RS	B2PLYP-COSMO-RS	DSD-PBEP86-COSMO-RS
1	silylated product	–11.49	–13.72	–27.87	–37.39
2	Cp_2TiCl_2	–12.40	–18.27	5.55	1.74
3	**Cp_2TiCl**	**0**	**0**	**0**	**0**
4	$[Cp_2TiCl_2{\bullet}HNEt_3]$	–7.44	–5.36	–5.04	
5	$Cp_2TiCl{\bullet}THF$	–2.61	–0.87	–2.39	
6	$[(Cp_2TiCl)_2]$	–9.48	–6.14	–7.94	–9.48
7	$[(Cp_2TiCl)_2ZnCl_2]$	–13.74	–10.45	–11.77	
8	$[Cp_2Ti(Cl)(BnCN)]$	–1.45	–1.61	–1.92	–2.35
9	$[Cp_2Ti(Cl)(PhCOMe)]$	3.78	4.15	5.79	7.23
10	bistitanated product	–0.78	–5.93	–21.82	–27.59
11	Ti-product radical complex	36.52	31.20	26.79	
12	$[Cp_2Ti(BnCN)_2{\bullet}Cl]$	14.04	11.62	11.12	
13	$[Cp_2Ti(BnCN)_2]^+$	12.84	14.10	11.68	
14	$[Cp_2Ti(BnCN)_2{\bullet}ZnCl_3(THF)]$	–4.07	–6.00	–8.01	
15	$[Cp_2Ti(BnCN)_2{\bullet}ZnCl_3(NEt_3)]$	–8.44	–9.17	–13.63	
17	$[Cp_2Ti]^+$	46.91	46.79	48.46	
18	$[Cp_2Ti(THF)]^+$	26.66	26.96	26.15	
19	$[Cp_2Ti(BnCN)]^+$	25.66	24.53	27.59	
20	$[Cp_2Ti(PhCOMe)]^+$	22.90	22.52	25.26	
21	$[Cp_2Ti(PhCOMe)(THF)]^+$	17.95	19.86	18.93	
22	$[Cp_2Ti(THF)_2]^+$	16.83	19.47	16.92	
23	$[Cp_2Ti(PhCOMe){\bullet}Cl{\bullet}(BnCN)TiCp_2]^+$	15.59	16.78	15.83	
24	$[Cp_2Ti(BnCN)(PhCOMe)]^+$	15.48	15.51	15.73	
25	$[Cp_2Ti(BnCN)(THF)]^+$	13.23	13.32	15.21	
26	bistitanated product cation 1	15.63	9.81	–9.98	
27	bistitanated product cation 2	20.72	14.77	–4.28	
28	Cl-bridged bistitanated product cation	20.63	16.56	–4.83	
TS-30	TS_prodti	17.48	16.91	–4.23	–6.65
30	monotitanated product	–3.77	–6.72	–20.38	–28.12
TS-31	TS_concerted	48.69	49.33	22.71	
31	product chelate	8.36	3.28	–11.31	
32	bistitanated product HCl complex	8.04	3.96	–14.52	–16.49
TS-33	TS_chloride shift to pentacoord.	13.21	11.88	–8.22	–9.98
33	bistitanated product pentacoord.	12.02	10.93	–10.74	–13.16
TS-34	TS_to prod. chelate HCl complex	12.08	10.64	–6.82	
34	product chelate HCl complex	1.84	–3.22	–17.31	
35	product chelate-$ZnCl_3$(THF) complex	–13.27	–12.73	–14.03	

Table S6. Single-point energies and Gibbs free energies in solution (Turbomole).

Identifier	Compound / Short Name	E_{el} / Hartree				$G°_{THF\text{-}BnCN}$ / kcal mol^{-1} [$= E_{el} + \mu + \Delta G°_{solv}$(COSMO-RS)]			
		PW6B95/ def2-QZVP	PBE0/ def2-QZVP	B2PLYP/ def2-QZVP	DSD-PBEP86/ def2-QZVPP	PW6B95	PBE0	B2PLYP	DSD-PBEP86
1	silylated product	–1160.429364	–1157.902134	–1158.241912	–1157.309857	–727981.79	–726395.93	–726609.14	–726024.27
2	Cp_2TiCl_2	–2159.140849	–2156.414217	–2156.672844	–2155.670900	–1354810.37	–1353099.39	–1353261.68	–1352632.95
3	Cp_2TiCl	–1698.506868	–1696.287606	–1696.500857	–1695.682287	–1065756.96	–1064364.35	–1064498.17	–1063984.50
4	$[Cp_2TiCl_2•HNEt_3]$	–2452.671465	–2449.221842	–2449.560893		–1538884.79	–1536720.11	–1536932.87	
5	$Cp_2TiCl•THF$	–1931.369836	–1928.593636	–1928.897989		–1211816.80	–1210074.71	–1210265.69	
6	$[(Cp_2TiCl)_2]$	–3397.061167	–3392.617317	–3393.046687	–3391.412001	–2131523.39	–2128734.84	–2129004.27	–2127978.49
7	$[(Cp_2TiCl)_2ZnCl_2]$	–6098.741101	–6092.133993	–6092.690364		–3826862.22	–3822716.20	–3823065.33	
8	$[Cp_2Ti(Cl)(BnCN)]$	–2062.966667	–2059.837945	–2060.205869	–2059.020470	–1294395.31	–1292432.01	–1292662.88	–1291919.04
9	$[Cp_2Ti(Cl)(PhCOMe)]$	–2084.083343	–2080.921834	–2081.290915	–2080.090843	–1307636.87	–1305653.00	–1305884.60	–1305131.54
10	bistitanated product	–4147.097477	–4140.815805	–4141.580239	–4139.205565	–2602035.29	–2598093.48	–2598573.17	–2597083.04
11	Ti-product radical complex	–2448.500273	–2444.438128	–2444.971016		–1536241.04	–1533692.00	–1534026.40	
12	$[Cp_2Ti(BnCN)_2•Cl]$	–2427.400250	–2423.365438	–2423.887818		–1523016.73	–1520484.84	–1520812.64	
13	$[Cp_2Ti(BnCN)_2]^+$	–1966.615007	–1963.081987	–1963.578791		–1233878.22	–1231661.21	–1231972.96	
14	$[Cp_2Ti(BnCN)_2•ZnCl_3(THF)]$	–5361.967375	–5355.214283	–5355.955519		–3364426.63	–3360189.00	–3360654.14	
15	$[Cp_2Ti(BnCN)_2•ZnCl_3(NEt_3)]$	–5422.054021	–5415.130920	–5415.886768		–3402076.70	–3397732.39	–3398206.69	
16	$Et_3N•HCl•ZnCl_2(THF)$	–3688.674546	–3684.729198	–3685.077413		–2314520.48	–2312044.74	–2312263.25	
17	$[Cp_2Ti]^+$	–1237.616043	–1235.904626	–1236.086562		–776570.34	–775496.41	–775610.58	
18	$[Cp_2Ti(THF)]^+$	–1470.521378	–1468.255123	–1468.529704		–922647.82	–921225.73	–921398.03	
19	$[Cp_2Ti(BnCN)]^+$	–1602.122569	–1599.503053	–1599.836942		–1005228.50	–1003584.73	–1003794.25	
20	$[Cp_2Ti(PhCOMe)]^+$	–1623.252221	–1620.599559	–1620.938228		–1018478.05	–1016813.48	–1017026.00	
21	$[Cp_2Ti(PhCOMe)(THF)]^+$	–1856.127215	–1852.916749	–1853.349959		–1164540.23	–1162525.63	–1162797.47	
22	$[Cp_2Ti(THF)_2]^+$	–1703.407028	–1700.582902	–1700.948921		–1068714.88	–1066942.71	–1067172.39	
23	$[Cp_2Ti(PhCOMe)•Cl•(BnCN)TiCp_2]^+$	–3686.271775	–3680.487650	–3681.199632		–2312879.21	–2309249.62	–2309696.40	
24	$[Cp_2Ti(BnCN)(PhCOMe)]^+$	–1987.733597	–1984.170586	–1984.667446		–1247122.37	–1244886.55	–1245198.33	
25	$[Cp_2Ti(BnCN)(THF)]^+$	–1835.011377	–1831.835759	–1832.260204		–1151298.15	–1149305.42	–1149571.76	
26	bistitanated product cation 1	–4050.742943	–4044.060283	–4044.956443		–2541516.08	–2537322.65	–2537885.00	
27	bistitanated product cation 2	–4050.727804	–4044.045334	–4044.940327		–2541510.99	–2537317.68	–2537879.30	
28	Cl-bridged bistitanated product cation	–3686.274808	–3680.499064	–3681.243619		–2312874.18	–2309249.84	–2309717.06	
TS-30	TS_Ti-N cleavage	–4608.290976	–4601.497205	–4602.296912	–4599.730469	–2891434.50	–2887171.34	–2887673.17	–2886062.70
30	monotitanated product	–2449.157165	–2445.093818	–2445.622985	–2444.066965	–1536645.38	–1534095.59	–1534427.64	–1533451.23
TS-31	TS_concerted	–4147.027058	–4140.736158	–4141.517692		–2601985.82	–2598038.22	–2598528.64	
31	product chelate	–1987.913996	–1984.358839	–1984.862571	–1983.488108	–1247215.78	–1244984.88	–1245300.98	
32	bistitanated product HCl complex	–4608.306362	–4601.518169	–4602.313641	–4599.746485	–2891443.95	–2887184.29	–2887683.46	–2886072.54
TS-33	TS_chloride shift to pentacoord.	–4608.300204	–4601.507635	–4602.305686	–4599.738191	–2891438.78	–2887176.37	–2887677.16	–2886066.03
33	bistitanated product pentacoord.	–4608.301702	–4601.508739	–4602.309304	–4599.742856	–2891439.96	–2887177.32	–2887679.68	–2886069.21

TS-34	TS_to prod. chelate HCl complex	–2449.132138	–2445.066382	–2445.601604		–1536629.52	–1534078.22	–1534414.08	
34	product chelate HCl complex	–2449.142188	–2445.082201	–2445.612052		–1536639.77	–1534092.09	–1534424.57	
35	product chelate-$ZnCl_3$(THF) complex	–5383.700815	–5376.922454	–5377.670823		–3378044.84	–3373791.36	–3374260.97	
	benzyl cyanide	–364.437976	–363.528273	–363.682442	–363.314925	–228636.90	–228066.06	–228162.80	–227932.18
	acetophenone	–385.559687	–384.618032	–384.776470	–384.397266	–241883.70	–241292.80	–241392.22	–241154.27
	Et_3N•HCl	–754.125728	–752.898677	–753.024977	–752.559536	–473120.39	–472350.41	–472429.66	–472137.59
	Et_3N	–292.913809	–292.191564	–292.290948	–292.011947	–183702.92	–183249.71	–183312.07	–183137.00
	$Zn(THF)_2Cl_2$	–3167.367834	–3164.096176	–3164.401298	–3163.264443	–1987449.03	–1985396.03	–1985587.50	–1984874.11
	$[Zn(THF)Cl_3]^-$	–3395.222444	–3391.997292	–3392.242381		–2130531.50	–2128507.69	–2128661.49	
	$ZnCl_4^{2-}$	–3622.947030	–3619.768905			–2273629.34	–2271635.03		
	TMSCl	–870.404117	–869.214767	–869.283229	–868.902405	–546139.06	–545392.73	–545435.69	–545196.72
	THF	–232.842182	–232.288028	–232.376705	–232.160598	–146057.23	–145709.49	–145765.14	–145629.53
	Zn	–1780.343922	–1779.185956	–1779.260930	–1778.916964	–1117215.34	–1116488.71	–1116535.75	–1116319.91

Table S7. Optimization results, ZPE, thermodynamic corrections (*freeh*) and COSMO-RS solvation energy (Turbomole).

Identifier	Compound / Short Name	Symmetry	E_{el}(TPSS-D3-COSMO/ def2-TZVP) / Hartree	ZPE / Hartree	Chem. pot. (μ) / kcal mol^{-1}	H / kcal mol^{-1}	S / cal mol^{-1} K^{-1}	ΔG^{o}_{solv}(COSMO-RS) / kcal mol^{-1}	Imaginary Frequencies
1	silylated product	C_1	–1159.202175084	0.3878897	209.99	258.97	0.16	–11.36	0
2	Cp_2TiCl_2	C_2	–2157.518786792	0.1705620	82.53	115.57	0.11	–11.56	0
3	Cp_2TiCl	C2	–1697.214471356	0.1677288	81.35	112.89	0.11	–9.15	0
4	$[Cp_2TiCl_2$•$HNEt_3]$	C_1	–2450.720325748	0.3868102	206.51	258.87	0.18	–16.71	0
5	Cp_2TiCl•THF	C_1	–1929.828361714	0.2848797	149.95	190.28	0.14	–13.87	0
6	$[(Cp_2TiCl)_2]$	D_2	–3394.467708498	0.3374792	179.56	227.19	0.16	–14.89	0
7	$[(Cp_2TiCl)_2ZnCl_2]$	C_2	–6094.516053393	0.3407312	173.75	233.01	0.20	–18.16	0
8	$[Cp_2Ti(Cl)(BnCN)]$	C_1	–2061.268393223	0.2947631	152.70	198.23	0.15	–16.88	0
9	$[Cp_2Ti(Cl)(PhCOMe)]$	C_1	–2082.374157004	0.3049294	160.11	204.74	0.15	–14.95	0
10	bistitanated product	C_1	–4143.696118640	0.6053986	333.74	405.68	0.24	–26.07	0
11	Ti-product radical complex	C_1	–2446.380730294	0.4332565	235.00	290.17	0.19	–18.92	0
12	$[Cp_2Ti(BnCN)_2$•$Cl]$	C_1	–2425.305826380	0.421651	224.82	283.56	0.20	–24.90	0
13	$[Cp_2Ti(BnCN)_2]^+$	C_1	–1964.885184882	0.4217083	226.99	282.18	0.19	–35.65	0
14	$[Cp_2Ti(BnCN)_2$•$ZnCl_3(THF)]$	C_1	–5357.978359345	0.5418141	287.39	366.94	0.27	–28.69	0
15	$[Cp_2Ti(BnCN)_2$•$ZnCl_3(NEt_3)]$	C_1	–5417.993127022	0.630358	341.39	425.20	0.28	–27.83	0
16	Et_3N•HCl•$ZnCl_2$(THF)	C_1	–3686.145994998	0.3386253	175.76	228.27	0.18	–18.02	0
17	$[Cp_2Ti]^+$	C_2	–1236.729233374	0.1667492	82.88	111.04	0.09	–37.42	0
18	$[Cp_2Ti(THF)]^+$	C_2	–1469.370876970	0.2842944	150.97	188.80	0.13	–32.69	0
19	$[Cp_2Ti(BnCN)]^+$	C_1	–1600.809262815	0.2940112	153.00	196.61	0.15	–34.41	0
20	$[Cp_2Ti(PhCOMe)]^+$	C_1	–1621.919585263	0.3045428	160.29	203.44	0.14	–32.19	0

21	$[Cp_2Ti(PhCOMe)(THF)]^+$	C_1	–1854.542900758	0.4223055	230.92	280.97	0.17	–33.74	0
22	$[Cp_2Ti(THF)_2]^+$	C_2	–1701.997411947	0.4026734	222.00	266.62	0.15	–32.83	0
23	$[Cp_2Ti(PhCOMe)•Cl•(BnCN)TiCp_2]^+$	C_1	–3683.227370900	0.6013332	330.14	403.18	0.24	–38.89	0
24	$[Cp_2Ti(BnCN)(PhCOMe)]^+$	C_1	–1985.987212177	0.4323167	234.40	288.98	0.18	–35.11	0
25	$[Cp_2Ti(BnCN)(THF)]^+$	C_1	–1833.442576742	0.4119543	223.10	274.37	0.17	–34.22	0
26	bistitanated product cation 1	C_1	–4047.308144109	0.7320699	407.55	489.62	0.28	–44.06	0
27	bistitanated product cation 2	C_1	–4047.299241367	0.7323958	407.85	489.73	0.27	–48.77	0
28	Cl-bridged bistitanated product cation	C_1	–3683.251993337	0.6051589	336.84	404.14	0.23	–38.65	0
TS-30	TS_prodti	C_1	–4604.539575406	0.6179011	339.48	414.76	0.25	–27.73	1 (–57.22 cm^{-1})
30	monotitanated product	C_1	–2447.034011927	0.4465368	243.09	298.50	0.19	–19.14	0
TS-31	TS_concerted	C_1	–4143.622078290	0.6047366	335.98	404.72	0.23	–23.03	1 (–44.01 cm^{-1})
31	product chelate	C_1	–1986.136625326	0.4320868	236.09	288.01	0.17	–17.01	0
32	bistitanated product HCl complex	C_1	–4604.563862570	0.6193286	340.90	415.73	0.25	–28.95	0
TS-33	TS_prodti2_pentacoord	C_1	–4604.552280499	0.618885	340.29	415.20	0.25	–27.03	1 (–59.98 cm^{-1})
33	bistitanated product pentacoord.	C_1	–4604.553039384	0.619149	339.83	415.84	0.25	–26.81	0
TS-34	TS_prodchelate HCl complex	C_1	–2447.007673150	0.4453118	242.70	297.44	0.18	–18.60	1 (–112.48 cm^{-1})
34	product chelate HCl complex	C_1	–2447.034521277	0.4468534	243.24	298.51	0.19	–23.08	0
35	product chelate $ZnCl_3(THF)$ complex	C_1	–5379.702517064	0.567142	306.38	381.93	0.25	–27.96	0
	benzyl cyanide	C_S	–364.028588839	0.1252597	57.75	84.00	0.09	–6.37	0
	acetophenone	C_S	–385.132546200	0.1356115	64.40	90.70	0.09	–5.74	0
	$Et_3N•HCl$	C_1	–753.483580454	0.2177421	112.85	144.52	0.11	–12.20	0
	Et_3N	C_1	–292.592145215	0.2021137	105.43	133.46	0.09	–2.16	0
	$Zn(THF)_2Cl_2$	C2	–3165.242936378	0.2362968	117.29	159.66	0.14	–12.99	0
	$[Zn(THF)Cl_3]^-$	C_1	–3393.061386629	0.1195821	48.11	83.65	0.12	–45.37	0
	$ZnCl_4^{2-}$	C_1	–3620.850142383	0.0035271	–20.62	8.07	0.10	–175.13	0
	TMSCl	C_S	–869.678352181	0.1111014	49.31	75.71	0.09	–1.54	0
	THF	C_S	–232.592349213	0.1151303	54.50	75.94	0.07	–1.05	0
	Zn	-	-	-	–9.99	-	-	–22.67 (= $-\Delta G_{vap}$)[a]	-

[a] Quasi-experimental free sublimation energy of zinc at 298.15 K, see above.

Table S8. Relative Gibbs free energy in solution for the C-C coupling transition states (ORCA). The energy (kcal mol^{-1}) is given in relation to the C-C coupling precursors.

Identifier	PW6B95-COSMO-RS	PBE0-COSMO-RS
TS-10-anti	14.2	12.8
TS-10-syn	20.2	17.9
TS-26	19.9	18.1
TS-27	23.1	20.0
TS-28	23.9	21.6

Table S9. Single-point energies and Gibbs free energies in solution for the C-C coupling precursors and the C-C coupling transition states (ORCA).

Identifier	E_{el} / Hartree		$G°_{THF\text{-}BnCN}$ / kcal mol^{-1} [= E_{el} + (G–E_{el}) + $\Delta G°_{solv}$(COSMO-RS)]	
	PW6B95/def2-QZVP	PBE0/def2-QZVP	PW6B95	PBE0
8	–2062.9657593542	–2059.8379659287	–1294390.25	–1292427.53
9	–2084.0821874678	–2080.9217795917	–1307634.04	–1305650.85
TS-10-anti	–4147.0622214650	–4140.7761980538	–2602010.10	–2598065.56
TS-10-syn	–4147.0491319454	–4140.7646994063	–2602004.06	–2598060.52
13	–1966.6138868059	–1963.0857873583	–1233872.12	–1231658.20
TS-26	–4050.7069290364	–4044.0212892369	–2541486.23	–2537290.93
24	–1987.7319303817	–1984.1703412933	–1247118.17	–1244883.24
TS-27	–4050.6947878692	–4044.0103651043	–2541485.35	–2537290.81
23	–3686.2692430411	–3680.4871728656	–2312873.00	–2309244.70
TS-28	–3686.2363598106	–3680.4580597718	–2312849.09	–2309223.15

From these values the relative energies of the C-C coupling transition states were calculated (PW6B95):

$$G°(\textbf{TS-10-anti}) - [G°(\textbf{8}) + G°(\textbf{9})] = 14.19 \text{ kcal mol}^{-1}$$
$$G°(\textbf{TS-10-syn}) - [G°(\textbf{8}) + G°(\textbf{9})] = 20.23 \text{ kcal mol}^{-1}$$
$$G°(\textbf{TS-26}) - [G°(\textbf{9}) + G°(\textbf{13})] = 19.93 \text{ kcal mol}^{-1}$$
$$G°(\textbf{TS-27}) - [G°(\textbf{8}) + G°(\textbf{24})] = 23.07 \text{ kcal mol}^{-1}$$
$$G°(\textbf{TS-28}) - G°(\textbf{23}) = 23.91 \text{ kcal mol}^{-1}$$

Table S10. Optimization results for the C-C coupling precursors and the C-C coupling transition states (ORCA).

Identifier	E_{el}(TPSS-D3-COSMO/def2-TZVP) / Hartree	ZPE / Hartree	G–E_{el} / kcal mol^{-1}	$\Delta G°_{solv}$(COSMO-RS) / kcal mol^{-1}	Imaginary Frequencies
8	–2061.26832	0.29386095	157.11	–16.80	0
9	–2082.374155	0.30421187	162.09	–14.81	0
TS-10-anti	–4143.659739	0.60018295	336.40	–25.66	1 (–75.51 cm^{-1})
TS-10-syn	–4143.652712	0.60016964	333.84	–25.28	1 (–231.24 cm^{-1})
13	–1964.888428	0.42040305	232.08	–35.35	0
TS-26	–4047.276426	0.72663244	412.26	–41.51	1 (–234.79 cm^{-1})
24	–1985.990500	0.43116898	237.33	–34.89	0
TS-27	–4047.272326	0.72743511	410.04	–46.03	1 (–167.69 cm^{-1})
23	–3683.230908	0.60008262	334.54	–38.67	0
TS-28	–3683.220023	0.60064457	337.24	–38.09	1 (–244.70 cm^{-1})

Appendix D — Coordinates (Turbomole)

1

```
47
Energy = -1159.202121330
N    -0.9444547   -1.0941086    2.5513154
O     1.3156283   -0.8803178    1.1798754
C     0.1827409   -1.1457934    0.3439572
C    -1.0477363   -1.1238634    1.2801085
C    -2.4168373   -1.1235292    0.6311495
C     0.2969817   -2.5510392   -0.2667264
H     1.1306625   -2.5911494   -0.9745169
H    -0.6148846   -2.8382370   -0.7967074
H     0.4741322   -3.2709026    0.5359998
H    -2.7040380    0.9053502    2.4389855
C    -3.0150301    1.2088060    1.4428876
C    -2.9318809    0.2890103    0.3903953
C    -3.3212127    0.6911820   -0.8905770
H    -3.2469158   -0.0115622   -1.7160437
C    -3.7731020    1.9905410   -1.1227909
H    -4.0574445    2.2907656   -2.1277156
C    -3.8456910    2.9047658   -0.0711773
H    -4.1908211    3.9193407   -0.2509214
C    -3.4683730    2.5074699    1.2141393
H    -3.5233470    3.2124705    2.0396202
C     0.0977474    1.2962893   -0.2486071
C    -0.0537408    2.3497829   -1.1434047
H    -0.0172469    3.3740882   -0.7834750
C    -0.2665820    2.0904089   -2.5005048
H    -0.3908278    2.9120409   -3.2003994
C    -0.3261369    0.7725327   -2.9489171
H    -0.4924770    0.5611255   -4.0017795
C    -0.1776088   -0.2845628   -2.0470332
H    -0.2321476   -1.3046697   -2.4133292
C     0.0384414   -0.0322110   -0.6911683
H    -3.1003240   -1.6577762    1.2995573
H    -2.3907418   -1.6531721   -0.3255776
H     0.2587955    1.4950775    0.8066401
H     0.0576139   -1.0493417    2.7897965
Si    2.9528285   -0.9332857    0.8200184
C     3.7149216    0.1873843    2.1127932
C     3.3240079   -0.3082910   -0.9107167
C     3.6024778   -2.6852423    1.0201706
H     3.3498666    1.2153025    2.0029433
H     4.8078539    0.2032071    2.0212923
H     3.4665967   -0.1545775    3.1246351
H     2.9644500    0.7161459   -1.0541221
H     2.8651716   -0.9343953   -1.6838835
H     4.4096814   -0.3179594   -1.0735379
H     3.3214234   -3.0973400    1.9967774
H     4.6981921   -2.6913882    0.9554010
H     3.2193871   -3.3583718    0.2451739
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2

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23
Energy = -2157.518786792
C    -1.2896463    2.0162247   -0.3021998
C    -1.1029413    1.3960527    0.9585023
C     0.2893283    1.4455747    1.2643558
C     0.9526855    2.0478724    0.1745972
H    -1.8823399    0.9854082    1.5849168
C    -0.0255425    2.3951297   -0.8005564
H    -2.2318199    2.1201492   -0.8181426
H     0.1721357    2.8299334   -1.7695395
Ti    0.0000000    0.0000000   -0.5956128
C    -0.9526855   -2.0478724    0.1745972
C     0.0255425   -2.3951297   -0.8005564
C    -0.2893283   -1.4455747    1.2643558
C     1.1029413   -1.3960527    0.9585023
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C     1.2896463   -2.0162247   -0.3021998
H    -0.7556914   -1.0728571    2.1648902
H    -2.0202194   -2.1846574    0.0780561
H    -0.1721357   -2.8299334   -1.7695395
H     1.8823399   -0.9854082    1.5849168
H     2.2318199   -2.1201492   -0.8181426
Cl   -1.7291260   -0.2468697   -2.1819693
Cl    1.7291260    0.2468697   -2.1819693
H     0.7556914    1.0728571    2.1648902
H     2.0202194    2.1846574    0.0780561
$symmetry c2
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3

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22
Energy = -1697.214226946
C    -2.3109050    0.4155528    0.8552778
C    -1.8447323    1.1854732   -0.2462600
C    -1.4420905    0.2753364   -1.2609103
C    -1.6293444   -1.0491613   -0.7752593
H    -1.8212145    2.2653895   -0.3095999
C    -2.1760824   -0.9577848    0.5292995
H    -2.6552564    0.8084957    1.8013717
H    -2.3995676   -1.7896835    1.1845279
Ti    0.0000000    0.0000000    0.5750510
C     1.6293444    1.0491613   -0.7752593
C     2.1760824    0.9577848    0.5292995
C     1.4420905   -0.2753364   -1.2609103
C     1.8447323   -1.1854732   -0.2462600
C     2.3109050   -0.4155528    0.8552778
H     1.0385502   -0.5465719   -2.2262548
H     1.3886706    1.9620601   -1.3044437
H     2.3995676    1.7896835    1.1845279
H     1.8212145   -2.2653895   -0.3095999
H     2.6552564   -0.8084957    1.8013717
Cl    0.0000000    0.0000000    2.9294511
H    -1.0385502    0.5465719   -2.2262548
H    -1.3886706   -1.9620601   -1.3044437
$symmetry c2
$alpha shells
 a       1-29                                   ( 1 )
 b       1-26                                   ( 1 )
$beta shells
 a       1-28                                   ( 1 )
 b       1-26                                   ( 1 )

<S*S>     0.75539563
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4

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46
Energy = -2450.720011340
C     1.7799809    2.2115839    0.7167937
C     2.8733387    1.6873710    1.4631641
C     3.9308301    1.4400353    0.5471874
C     3.4765177    1.7652803   -0.7621859
C     2.1528307    2.2632549   -0.6419067
Ti    2.2062239   -0.0726119    0.0406796
C     4.1730518   -1.3961901   -0.3355228
C     3.8656520   -1.4923716    1.0539791
C     2.6156701   -2.1330102    1.1821340
C     2.1333660   -2.4177198   -0.1255981
C     3.1109513   -1.9760695   -1.0617665
Cl    0.0723732   -0.3139334    1.4133680
H     4.9097214    1.0584824    0.7991362
H     4.0391957    1.6627950   -1.6805592
H     1.5147966    2.5554855   -1.4626650
H     0.8097754    2.4650942    1.1184097
H     2.8960831    1.5192417    2.5315715
H     2.0893431   -2.3190090    2.1073393
H     1.1750657   -2.8542650   -0.3676684
H     3.0257797   -2.0223263   -2.1379026
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H     5.0541965   -0.9346211   -0.7606759
H     4.4714925   -1.1165684    1.8675307
Cl    0.7173878   -0.1407600   -1.9654061
N    -2.6067676    0.0172930   -0.1075583
C    -2.5600013    0.8307315   -1.3812367
H    -1.9670179    0.2474291   -2.0838297
H    -3.5909250    0.9083115   -1.7384413
C    -3.4115904    0.7263614    0.9606987
H    -2.9162326    1.6844353    1.1173800
H    -4.3997052    0.9097903    0.5294615
C    -3.1116504   -1.3875532   -0.3469515
H    -3.0683619   -1.8854908    0.6215411
H    -4.1591699   -1.2974418   -0.6486423
C    -1.9057610    2.1899014   -1.1828610
H    -1.7608114    2.6417324   -2.1682456
H    -2.5126932    2.8735623   -0.5841878
H    -0.9210719    2.0674270   -0.7239094
C    -3.4990726   -0.0345884    2.2766913
H    -3.9457848    0.6332843    3.0192358
H    -4.1293326   -0.9240872    2.2056188
H    -2.5050095   -0.3224915    2.6304845
C    -2.2788831   -2.1565045   -1.3626763
H    -2.5648485   -3.2109784   -1.3061330
H    -2.4477282   -1.8145897   -2.3862668
H    -1.2121130   -2.0650926   -1.1391027
H    -1.6190922   -0.0706095    0.2594944

<S*S>     0.75563150
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5

```
35
Energy = -1929.828044258
C    -0.7530950    2.3797433   -0.4322211
C    -2.0873077    2.0533554   -0.8143138
C    -2.6912304    1.3825455    0.2742874
C    -1.7337881    1.2813597    1.3260686
H    -2.5434488    2.2617502   -1.7719015
C    -0.5500278    1.9186820    0.8916859
H    -0.0192354    2.8657554   -1.0587617
H     0.3703512    1.9954957    1.4551842
Ti   -0.9346395    0.0162429   -0.5532209
C    -1.5062929   -2.0445450   -1.7027392
C    -0.5912181   -2.3569183   -0.6736394
C    -2.6783704   -1.5126999   -1.1121803
C    -2.4941106   -1.5309117    0.3001960
C    -1.1972054   -2.0362816    0.5759219
H    -3.5545376   -1.1587865   -1.6393363
H    -1.3142888   -2.1246341   -2.7621865
H     0.4156658   -2.7249897   -0.8178429
H    -3.2144146   -1.2108510    1.0391413
H    -0.7688485   -2.1842260    1.5577798
H    -3.7007751    0.9968564    0.2965694
H    -1.8848725    0.7979066    2.2822440
C     3.5555484    0.1757885    0.0353616
C     2.3152490    0.5784898   -0.7463524
O     1.2166452   -0.1472288   -0.0946288
C     1.6520602   -0.6223366    1.2227886
C     3.0074434    0.0306755    1.4621547
H     4.3462811    0.9258041   -0.0446766
H     3.9419048   -0.7825787   -0.3273012
H     2.3083925    0.2858247   -1.7942221
H     2.1058978    1.6505877   -0.6656231
H     1.7214374   -1.7134930    1.1701712
H     0.8861615   -0.3396234    1.9479815
H     3.6417290   -0.5789846    2.1101179
H     2.8819902    1.0159651    1.9235476
Cl   -0.1490500    0.4562603   -2.8600540

<S*S>     0.75557596
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6 (triplet)

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44
Energy = -3394.467537021
C     0.4488512   -2.3270093    1.7351878
C     1.2529797   -1.8061843    2.7902152
C     0.3785880   -1.3970241    3.8262725
C    -0.9614848   -1.6361523    3.4044146
H     2.3324308   -1.7396052    2.7980650
C    -0.9083341   -2.2305773    2.1216848
H     0.8186445   -2.6958811    0.7909946
H    -1.7626308   -2.5010606    1.5174518
Ti    0.0000000    0.0000000    1.9608664
C     0.9083341    2.2305773    2.1216848
C    -0.4488512    2.3270093    1.7351878
C     0.9614848    1.6361523    3.4044146
C    -0.3785880    1.3970241    3.8262725
C    -1.2529797    1.8061843    2.7902152
H     1.8585708    1.4046805    3.9632433
H     1.7626308    2.5010606    1.5174518
H    -0.8186445    2.6958811    0.7909946
H    -0.6788853    0.9623890    4.7689064
H    -2.3324308    1.7396052    2.7980650
Cl   -1.6142485    0.0000000    0.0000000
H     0.6788853   -0.9623890    4.7689064
H    -1.8585708   -1.4046805    3.9632433
Cl    1.6142485    0.0000000    0.0000000
Ti    0.0000000    0.0000000   -1.9608664
C    -0.4488512   -2.3270093   -1.7351878
C     0.9083341   -2.2305773   -2.1216848
C     0.9614848   -1.6361523   -3.4044146
C    -0.3785880   -1.3970241   -3.8262725
C    -1.2529797   -1.8061843   -2.7902152
H     1.7626308   -2.5010606   -1.5174518
H     1.8585708   -1.4046805   -3.9632433
H    -0.6788853   -0.9623890   -4.7689064
H    -2.3324308   -1.7396052   -2.7980650
H    -0.8186445   -2.6958811   -0.7909946
C     0.4488512    2.3270093   -1.7351878
C     1.2529797    1.8061843   -2.7902152
C     0.3785880    1.3970241   -3.8262725
C    -0.9614848    1.6361523   -3.4044146
C    -0.9083341    2.2305773   -2.1216848
H    -1.7626308    2.5010606   -1.5174518
H     0.8186445    2.6958811   -0.7909946
H     2.3324308    1.7396052   -2.7980650
H     0.6788853    0.9623890   -4.7689064
H    -1.8585708    1.4046805   -3.9632433
$symmetry d2
$alpha shells
 a       1-29                                   ( 1 )
 b1      1-28                                   ( 1 )
 b2      1-26                                   ( 1 )
 b3      1-27                                   ( 1 )
$beta shells
 a       1-28                                   ( 1 )
 b1      1-27                                   ( 1 )
 b2      1-26                                   ( 1 )
 b3      1-27                                   ( 1 )

<S*S>     2.01197895
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7 (triplet)

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47
Energy = -6094.515900680
C    -2.4274737    2.2371856    0.7790446
C    -3.8009402    2.4171682    0.4566763
C    -4.5511668    1.5455344    1.2935458
C    -3.6414415    0.7978299    2.0935342
H    -4.2006053    3.1041714   -0.2772220
C    -2.3308189    1.2493750    1.7825888
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H    -1.5977819    2.7385385    0.3039875
H    -1.4125175    0.8658729    2.2023161
Ti   -3.3152243    0.2078777   -0.1570601
C    -4.5703251   -0.3050215   -2.0979080
C    -3.8533339   -1.4652056   -1.6903883
C    -5.5012697    0.0083493   -1.0847108
C    -5.3791301   -0.9698752   -0.0538446
C    -4.3714282   -1.8837019   -0.4308419
H    -6.1744103    0.8548895   -1.0813476
H    -4.3983825    0.2645180   -3.0001401
H    -3.0406244   -1.9306119   -2.2292041
H    -5.9451232   -0.9959579    0.8674251
H    -4.0254097   -2.7254286    0.1525498
Cl   -1.6877469    1.0181585   -2.0190906
Cl   -1.3345785   -1.3780547    0.3945381
H    -5.6277880    1.4594647    1.3131706
H    -3.9003759    0.0389323    2.8197452
Zn    0.0000000    0.0000000   -0.8640900
Cl    1.3345785    1.3780547    0.3945381
Cl    1.6877469   -1.0181585   -2.0190906
Ti    3.3152243   -0.2078777   -0.1570601
C     2.3308189   -1.2493750    1.7825888
C     3.6414415   -0.7978299    2.0935342
C     4.5511668   -1.5455344    1.2935458
C     3.8009402   -2.4171682    0.4566763
C     2.4274737   -2.2371856    0.7790446
H     3.9003759   -0.0389323    2.8197452
H     5.6277880   -1.4594647    1.3131706
H     4.2006053   -3.1041714   -0.2772220
H     1.5977819   -2.7385385    0.3039875
H     1.4125175   -0.8658729    2.2023161
C     4.3714282    1.8837019   -0.4308419
C     5.3791301    0.9698752   -0.0538446
C     5.5012697   -0.0083493   -1.0847108
C     4.5703251    0.3050215   -2.0979080
C     3.8533339    1.4652056   -1.6903883
H     3.0406244    1.9306119   -2.2292041
H     4.0254097    2.7254286    0.1525498
H     5.9451232    0.9959579    0.8674251
H     6.1744103   -0.8548895   -1.0813476
H     4.3983825   -0.2645180   -3.0001401
$symmetry c2
$alpha shells
 a       1-72                                   ( 1 )
 b       1-70                                   ( 1 )
$beta shells
 a       1-71                                   ( 1 )
 b       1-69                                   ( 1 )

<S*S>     2.01213449
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8

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38
Energy = -2061.268053099
C    -2.2390745   -2.9160820    0.8662522
C    -3.4881813   -2.2556508    0.7807535
C    -3.6790791   -1.8650897   -0.5773174
C    -2.5309751   -2.2469106   -1.3166942
H    -4.1770696   -2.0854090    1.5976623
C    -1.6418991   -2.9042506   -0.4137746
H    -1.7857201   -3.2947060    1.7701000
H    -0.6641117   -3.2955786   -0.6580090
Ti   -1.8608732   -0.6116740    0.2237558
C    -2.5584951    1.3609364    1.3280805
C    -1.4417273    1.6833135    0.5059685
C    -3.6219540    0.9758968    0.4807908
C    -3.1717848    1.0696258   -0.8687404
C    -1.8333811    1.5180003   -0.8519434
H    -4.6008111    0.6445435    0.8007891
H    -2.5716187    1.3611347    2.4085922
```

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H    -0.4595387    1.9684707    0.8551614
H    -3.7468665    0.8244835   -1.7511694
H    -1.2045370    1.6669656   -1.7189829
Cl   -0.4503727   -0.8150471    2.2642626
N     0.0323603   -0.6266344   -0.7338902
H    -4.5465339   -1.3548632   -0.9704961
H    -2.3626494   -2.0789613   -2.3721940
C     1.1195904   -0.5633731   -1.1285107
C     2.5181868   -0.4381402   -1.5014272
C     3.2777671    0.4778845   -0.5439941
H     2.5820938   -0.0604572   -2.5280899
H     2.9552791   -1.4458553   -1.5028239
C     4.4330256    1.1201465   -1.0010248
C     2.8569709    0.6642822    0.7762297
C     3.5933693    1.4843364    1.6333477
C     4.7497821    2.1203642    1.1791274
C     5.1680939    1.9364817   -0.1408047
H     4.7570717    0.9839417   -2.0299606
H     6.0637399    2.4324772   -0.5040993
H     3.2580499    1.6263291    2.6568645
H     5.3197291    2.7597392    1.8471637
H     1.9521440    0.1793297    1.1390450

<S*S>     0.75540579
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9

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39
Energy = -2082.373888803
C     2.0254693   -1.5364907   -0.5759991
C     3.2015918   -0.7609680   -0.7023604
C     3.7415505   -0.5594940    0.5995753
C     2.9085397   -1.2348303    1.5223895
H     3.6101122   -0.3773807   -1.6263149
C     1.8425047   -1.8270829    0.8047551
H     1.3689112   -1.8248834   -1.3853606
H     1.0078842   -2.3596067    1.2387570
Ti    1.6129312    0.5383131    0.5132597
C     0.7258727    2.3777301   -0.7670214
C     1.1042606    2.8836076    0.4955317
C     1.8889613    1.8990760   -1.4196154
C     3.0001127    2.1562470   -0.5663005
C     2.5166222    2.7408045    0.6244718
H     1.9250401    1.4338840   -2.3954459
H    -0.2810098    2.3121191   -1.1548237
H     0.4439166    3.2809431    1.2512065
H     4.0317678    1.9164036   -0.7805042
H     3.1058522    3.0155873    1.4882273
O    -0.2680166   -0.0841342    0.2884945
Cl    1.1712498    0.8854844    2.8871371
H     4.6249793    0.0152836    0.8431347
H     3.0301691   -1.2425129    2.5950959
C    -1.5129139    0.1761885    0.3909316
C    -1.9724690    1.4334341    1.0701097
H    -1.1632138    1.8127384    1.6947657
H    -2.8515432    1.2459587    1.6932892
H    -2.2520367    2.2002639    0.3348222
C    -2.4590050   -0.7786044   -0.1687762
C    -3.8510323   -0.5407115   -0.1469419
H    -4.2402572    0.3704900    0.2952906
C    -4.7353970   -1.4644234   -0.6951930
H    -5.8031096   -1.2655058   -0.6715462
C    -4.2567046   -2.6441865   -1.2735950
H    -4.9501656   -3.3641361   -1.6983589
C    -2.8781896   -2.8920641   -1.3034918
H    -2.5011179   -3.8070813   -1.7518499
C    -1.9900266   -1.9722966   -0.7631779
H    -0.9220908   -2.1581634   -0.7845682

<S*S>     0.75860414
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10

77

Energy = -4143.695789088

Ti	-3.5231869	-0.2480003	-0.7517316
Ti	3.5565199	-0.5128569	-0.1665739
N	-1.7258804	0.0245325	-0.2551772
O	1.8109565	0.1004553	-0.1614888
C	0.6199611	0.4000506	-0.8527971
C	-0.5698751	0.2636166	0.1656786
C	-0.2630931	0.4759831	1.6434524
Cl	-3.1701585	-0.0593161	-3.1754131
C	0.3863250	-0.5702325	-2.0165513
H	1.0346818	-0.3303613	-2.8604541
H	-0.6556900	-0.5180277	-2.3408566
H	0.6050811	-1.5849217	-1.6736715
C	-4.6651631	1.0403827	0.8787790
C	-3.5937989	1.8443755	0.4189944
C	-5.5749884	0.8646179	-0.2066649
C	-5.0387369	1.5185953	-1.3336614
C	-3.8040696	2.1182302	-0.9517244
H	-5.4639932	1.5251343	-2.3264435
H	-3.1308447	2.6577068	-1.6011175
H	-2.7405500	2.1528716	1.0044609
H	-4.7784681	0.6479279	1.8797588
H	-6.4967141	0.3002694	-0.1773322
C	-4.9639728	-2.1292519	-0.9099166
C	-4.6777420	-1.9172149	0.4701674
C	-3.2969453	-2.1370607	0.6723494
C	-2.7268165	-2.5049763	-0.5809346
C	-3.7585557	-2.5179221	-1.5448159
H	-1.6820155	-2.7091099	-0.7636999
H	-3.6380238	-2.7212233	-2.5975991
H	-5.9278942	-2.0173151	-1.3879586
H	-5.3921092	-1.6293311	1.2279067
H	-2.7630331	-2.0305050	1.6048442
C	3.7439795	-0.8419217	-2.5415049
C	3.5250656	0.5335404	-2.3399647
C	4.6189994	1.0535326	-1.6015523
C	5.5581206	-0.0017563	-1.4182155
C	5.0074674	-1.1749661	-1.9667123
H	6.5086131	0.0789632	-0.9119093
H	5.4470408	-2.1619106	-1.9349242
H	3.0651536	-1.5378797	-3.0106099
H	2.6508723	1.0970191	-2.6298947
H	4.7345602	2.0780125	-1.2752669
C	4.9433276	0.6778241	1.3831599
C	5.3577744	-0.6839922	1.4382490
C	4.2910578	-1.4361955	1.9781435
C	3.2201769	-0.5525584	2.2598655
C	3.6264535	0.7531132	1.9000152
H	2.2502043	-0.8410015	2.6372189
H	3.0261996	1.6501526	1.9678854
H	5.5340211	1.5109136	1.0297946
H	6.3113303	-1.0783169	1.1167552
H	4.2792244	-2.5067475	2.1160426
Cl	2.9325792	-2.8297482	-0.3209051
H	-1.9153332	0.2155476	3.8019298
C	-1.4575276	-0.7301424	3.5213812
C	-0.5695255	-0.7698097	2.4414502
C	0.0014899	-1.9983580	2.0779922
H	0.6872478	-2.0463731	1.2351202
C	-0.3099197	-3.1595828	2.7826865
H	0.1369344	-4.1046006	2.4859965
C	-1.2005344	-3.1124675	3.8592255
H	-1.4500844	-4.0195352	4.4024500
C	-1.7718273	-1.8935272	4.2285691
H	-2.4688629	-1.8478453	5.0609525
C	1.4693246	2.7997342	-0.7108825
C	1.4136218	4.1437032	-1.0837336
H	2.1021430	4.8555299	-0.6360481
C	0.4797972	4.5709917	-2.0288877

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H     0.4364138    5.6162345   -2.3221077
C    -0.3991201    3.6439757   -2.5958728
H    -1.1306024    3.9677057   -3.3317867
C    -0.3450839    2.3013353   -2.2238076
H    -1.0469929    1.5921786   -2.6549061
C     0.5985386    1.8668756   -1.2826890
H    -0.8753533    1.3066066    2.0098623
H     0.7887547    0.7543283    1.7438753
H     2.2030739    2.4642954    0.0137527
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11

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55
Energy = -2446.380526943
Ti    1.7981436   -1.0055839    0.3624391
N    -3.6404315   -0.9507865    0.1161531
O    -0.0563926   -0.8119188    0.2180893
C    -1.2367840   -1.2205390   -0.4068468
C    -2.4740360   -0.8336364    0.5344286
C    -2.1707803   -0.3894987    1.9584796
C    -1.2922145   -2.7538002   -0.5130187
H    -0.5259231   -3.1164998   -1.2000954
H    -2.2755270   -3.0794843   -0.8580705
H    -1.1034284   -3.1828761    0.4740148
C     2.2141163   -2.7250806   -1.2876999
C     1.5708113   -1.6738801   -1.9628595
C     2.4025337   -0.5244549   -1.8927067
C     3.6044766   -0.9024152   -1.2369412
C     3.4747317   -2.2439456   -0.8221334
H     4.4526905   -0.2590581   -1.0591672
H     4.1939790   -2.8074832   -0.2439297
H     1.8155109   -3.7128762   -1.1113059
H     0.5931993   -1.7039445   -2.4185891
H     2.1765761    0.4494859   -2.3043486
C     2.7241259    1.1627062    0.7193998
C     3.5927256    0.2520827    1.3956358
C     2.8640133   -0.3386242    2.4450422
C     1.5513927    0.2060224    2.4353836
C     1.4772534    1.1519771    1.3897457
H     0.7459376   -0.0850046    3.0917918
H     0.5971361    1.7101960    1.1048389
H     2.9819634    1.7735304   -0.1347311
H     4.6219560    0.0399499    1.1457019
H     3.2271975   -1.1028364    3.1157610
Cl    1.6657251   -2.9963887    1.6946309
H    -1.2496681    0.9209952    4.1281620
C    -1.4130290    1.6005648    3.2950238
C    -1.8981073    1.0991839    2.0793115
C    -2.1191948    1.9920919    1.0267817
H    -2.5149752    1.6281865    0.0838306
C    -1.8286619    3.3510922    1.1714922
H    -1.9955699    4.0268100    0.3370970
C    -1.3260810    3.8374546    2.3781306
H    -1.0954294    4.8929722    2.4906235
C    -1.1277539    2.9562352    3.4445783
H    -0.7444546    3.3243144    4.3922657
C    -0.8093093    0.7572649   -1.9310169
C    -0.9847313    1.4571736   -3.1238681
H    -0.5002201    2.4204289   -3.2590375
C    -1.7783421    0.9220946   -4.1405373
H    -1.9139462    1.4634515   -5.0725271
C    -2.3954175   -0.3153947   -3.9500301
H    -3.0141503   -0.7425847   -4.7343671
C    -2.2204014   -1.0142711   -2.7541284
H    -2.7108961   -1.9729560   -2.6238301
C    -1.4203650   -0.4858322   -1.7350751
H    -1.2971641   -0.9527202    2.3037424
H    -3.0247651   -0.6607661    2.5875498
H    -0.1880449    1.1688764   -1.1432637

<S*S>     0.75813949
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12

54
Energy = -2425.304935136

C	-2.2502226	-2.2730886	0.6107978
C	-3.3717963	-1.8755545	1.3986994
C	-4.4814717	-1.7468231	0.5292423
C	-4.0504809	-2.0585613	-0.7935887
H	-3.3703884	-1.6920502	2.4646604
C	-2.6806103	-2.4001130	-0.7351355
H	-1.2451277	-2.4371189	0.9740270
H	-2.0565566	-2.6601215	-1.5787610
Ti	-2.8914201	-0.1092699	-0.0668239
C	-2.8797910	2.1489474	-0.7274975
C	-3.7169725	1.4228044	-1.6271827
C	-3.4940242	2.1173126	0.5513702
C	-4.6839377	1.3582758	0.4600307
C	-4.8294264	0.9403263	-0.8951465
H	-3.0953089	2.5579313	1.4546942
H	-1.9263204	2.6113771	-0.9728746
H	-3.5247532	1.2567235	-2.6788453
H	-5.3628977	1.1361302	1.2725652
H	-5.6418758	0.3454964	-1.2893807
N	-1.1774158	-0.0542638	-1.3037940
H	-5.4806125	-1.4485490	0.8147726
H	-4.6620530	-2.0359045	-1.6854723
C	-0.1657650	0.0929485	-1.8473928
C	1.1323672	0.2995106	-2.4533945
C	2.2142650	-0.6064068	-1.8858839
H	1.3502846	1.3706832	-2.2718808
H	1.0406783	0.1683369	-3.5380524
C	2.0291821	-1.3495930	-0.7180033
C	3.4495455	-0.6577811	-2.5409259
C	4.4843544	-1.4407450	-2.0307891
C	4.2941908	-2.1830158	-0.8632588
C	3.0638447	-2.1342775	-0.2086265
H	1.0785414	-1.3052163	-0.1941569
H	2.9093635	-2.6984598	0.7064071
H	5.4403999	-1.4700422	-2.5461592
H	5.1020102	-2.7898009	-0.4643193
H	3.6023970	-0.0787011	-3.4482484
H	0.3041631	2.0805202	3.3643767
H	1.1910178	2.3441486	0.6094324
N	-1.4394336	0.3831154	1.4028046
C	-0.5819152	0.6840622	2.1214236
C	0.5255187	1.0763979	2.9797736
C	2.0147915	1.7835211	1.0494451
H	0.5506405	0.3966230	3.8381685
C	1.8556741	1.0566231	2.2327620
H	3.3505835	2.3444780	-0.5281653
C	3.2453630	1.7808118	0.3941542
C	2.9259484	0.3211486	2.7481153
C	4.3184652	1.0541894	0.9118465
H	2.7984932	-0.2524005	3.6631427
C	4.1565124	0.3229233	2.0888269
H	5.2718417	1.0438028	0.3920626
H	4.9833289	-0.2555867	2.4911074
Cl	0.3768108	3.5142754	-1.6309491

<S*S> 0.75566644

13

53
Energy = -1964.883792760

C	-0.3390878	-2.7482986	0.3153592
C	-1.5576768	-2.4899831	1.0111235
C	-2.6108200	-2.5464190	0.0673464
C	-2.0492586	-2.8357998	-1.2107919
H	-1.6576024	-2.2759079	2.0667785
C	-0.6528488	-2.9784881	-1.0495651
H	0.6518888	-2.7585818	0.7477661

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H     0.0581009   -3.1813646   -1.8383265
Ti   -1.2215638   -0.7232407   -0.4937251
C    -1.4943506    1.5018721   -1.2167322
C    -2.1154052    0.6474142   -2.1755561
C    -2.2184113    1.3952854   -0.0005589
C    -3.2628882    0.4625867   -0.1890033
C    -3.2068150    0.0094236   -1.5394382
H    -1.9859398    1.9066837    0.9229976
H    -0.6208635    2.1172212   -1.3838106
H    -1.8008193    0.5029162   -3.2002959
H    -3.9785350    0.1502040    0.5592660
H    -3.8767664   -0.7066595   -1.9943565
N     0.5318920   -0.4661902   -1.6528109
H    -3.6595800   -2.3875526    0.2756781
H    -2.5945636   -2.9326091   -2.1397723
C     1.4324361   -0.1622407   -2.3161590
C     2.4745399    0.3685671   -3.1846790
C     2.0298831    1.7504932   -3.6552931
H     2.6177943   -0.3172207   -4.0262271
H     3.4134221    0.4163197   -2.6229640
C     1.2839330    1.8833840   -4.8295968
C     2.3157412    2.8786286   -2.8808625
C     1.8632148    4.1354657   -3.2839743
C     1.1196026    4.2678694   -4.4585566
C     0.8328520    3.1411081   -5.2317769
H     1.0578927    1.0060421   -5.4302076
H     0.2588685    3.2401125   -6.1483957
H     2.0927920    5.0098568   -2.6821021
H     0.7676172    5.2463418   -4.7718738
H     2.8931571    2.7759287   -1.9655118
H     2.4252584    0.6226771    3.0004619
H     2.8156446   -1.6501249    3.8066309
N    -0.0235630   -0.0067212    1.0988702
C     0.6169677    0.3014515    2.0145166
C     1.3566216    0.5861235    3.2367626
C     1.9127538   -1.5893689    4.4088928
H     1.0583781    1.5770650    3.5965968
C     1.0524822   -0.4977599    4.2663160
H     2.2918714   -3.4400070    5.4401460
C     1.6163889   -2.5969325    5.3282711
C    -0.1092610   -0.4214455    5.0404424
C     0.4572941   -2.5192261    6.1022176
H    -0.7807212    0.4263233    4.9290585
C    -0.4045686   -1.4295090    5.9579926
H     0.2276098   -3.3031749    6.8178680
H    -1.3049889   -1.3625388    6.5615645

<S*S>     0.75587762
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14

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70
Energy = -5357.977960882
Zn    2.3138053   -2.6114702    0.5598926
Ti   -0.0492092    1.8201818   -2.2808318
Cl    3.7436693   -1.2292529   -0.5306889
Cl    2.7983805   -2.7735817    2.7595315
Cl    0.1182700   -2.5069191    0.0598523
N    -1.4593921    0.7294657   -1.1290005
N     1.0866498    1.4599867   -0.5302015
C     0.4757656   -0.3631590   -2.9519528
H     0.3158597   -1.1626231   -2.2396495
C     1.6742457    0.3843697   -3.0882203
H     2.5674661    0.2328392   -2.4972982
C     1.4615453    1.3856181   -4.0627238
H     2.1806937    2.1294551   -4.3787541
C     0.1319533    1.2406401   -4.5584219
H    -0.3303596    1.8562458   -5.3176644
C    -0.4796941    0.1630067   -3.8724486
H    -1.4949504   -0.1853564   -4.0083655
C    -0.6967647    3.6896717   -1.0130330
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H    -0.7485566    3.5958689    0.0631517
C     0.4581767    4.0561963   -1.7655824
H     1.4335381    4.2922990   -1.3622214
C     0.1070852    4.0227866   -3.1356140
H     0.7656907    4.2371044   -3.9657535
C    -1.2619783    3.6390426   -3.2355968
H    -1.8234362    3.5120535   -4.1510349
C    -1.7585633    3.4507449   -1.9266713
H    -2.7613105    3.1356987   -1.6724321
C    -2.0852913    0.1204384   -0.3692274
C    -2.8542106   -0.6091572    0.6209769
H    -2.1359873   -1.2128054    1.1920800
H    -3.5108094   -1.3124896    0.0942436
C    -3.6613452    0.2921357    1.5462646
C    -3.5841041    1.6836449    1.4908275
H    -2.9341326    2.1614129    0.7640089
C    -4.3240482    2.4679400    2.3775387
H    -4.2501369    3.5504580    2.3276018
C    -5.1461250    1.8638890    3.3273875
H    -5.7198388    2.4726835    4.0201638
C    -5.2253070    0.4698985    3.3865303
H    -5.8610541   -0.0094521    4.1255368
C    -4.4876665   -0.3124028    2.5002073
H    -4.5479648   -1.3965430    2.5526470
C     1.5172530    1.1912096    0.5106603
C     1.9090637    0.8967394    1.8808341
H     2.6802885    1.6143053    2.1831892
H     2.3574246   -0.1029344    1.9115392
C     0.6808993    0.9787030    2.7820979
C     0.1811483    2.2225711    3.1815436
H     0.6804054    3.1347415    2.8627494
C    -0.9527461    2.2945251    3.9903868
H    -1.3389261    3.2633565    4.2937282
C    -1.5929512    1.1246659    4.4025894
H    -2.4833682    1.1810645    5.0207842
C    -1.0964097   -0.1159203    4.0022076
H    -1.5927449   -1.0291585    4.3179944
C     0.0362312   -0.1919499    3.1896923
H     0.4252177   -1.1563744    2.8769655
C     3.7649644   -5.3577177   -2.2863341
C     2.5910292   -4.5757919   -1.7128323
O     2.8853680   -4.4459216   -0.2734552
C     4.2832134   -4.8436050   -0.0213730
C     4.9307985   -4.8979745   -1.3964431
H     3.9208419   -5.1321876   -3.3442709
H     3.6006401   -6.4349151   -2.1775867
H     1.6247280   -5.0752723   -1.7950243
H     2.5280864   -3.5664531   -2.1319780
H     4.2554519   -5.8222575    0.4676747
H     4.7159381   -4.1028730    0.6531601
H     5.7826458   -5.5822395   -1.4207961
H     5.2649504   -3.8988993   -1.6927575

<S*S>     0.75561841
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15

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79
Energy = -5417.992830099
Zn    2.3930233   -1.8858952    0.3305738
Ti   -0.4855120    2.4705452   -2.2920318
Cl    3.6577241   -0.2324095   -0.6289246
Cl    2.8998827   -1.9904871    2.5545045
Cl    0.1707384   -1.5627518   -0.0656618
N    -1.8177509    1.3225128   -1.1009645
N     0.7178956    2.1350947   -0.5831578
N     2.8400150   -3.7408228   -0.5897295
C    -0.2853962    0.2773463   -3.2104293
H    -0.7242885   -0.5621985   -2.6908579
C     1.0279965    0.7554800   -3.0041535
H     1.7440844    0.3479381   -2.3013524
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C	1.2115584	1.9077260	-3.8142391
H	2.1088947	2.5098393	-3.8728342
C	0.0072951	2.1202090	-4.5446740
H	-0.1675849	2.9084609	-5.2632233
C	-0.9303438	1.1241094	-4.1556450
H	-1.9441641	1.0227612	-4.5203057
C	-1.2666143	4.2603437	-0.9962774
H	-1.3860662	4.1129623	0.0684158
C	-0.0812822	4.7070386	-1.6484399
H	0.8553667	4.9541499	-1.1678998
C	-0.3311696	4.7200654	-3.0388820
H	0.3799329	4.9883878	-3.8083191
C	-1.6752839	4.2946581	-3.2528120
H	-2.1621478	4.1835523	-4.2121873
C	-2.2547780	4.0237186	-1.9936260
H	-3.2592309	3.6603240	-1.8244254
C	-2.3682339	0.6699724	-0.3196398
C	-3.0332225	-0.1351976	0.6868619
H	-2.2389471	-0.6404426	1.2531779
H	-3.6044298	-0.9184456	0.1734265
C	-3.9321738	0.6656520	1.6185482
C	-4.0338725	2.0550023	1.5496725
H	-3.4690396	2.6029101	0.8010679
C	-4.8462460	2.7491957	2.4481664
H	-4.9122659	3.8317131	2.3872776
C	-5.5635349	2.0561074	3.4221768
H	-6.1934892	2.5949855	4.1239578
C	-5.4665435	0.6637431	3.4921545
H	-6.0205846	0.1157280	4.2489751
C	-4.6554041	-0.0281796	2.5949760
H	-4.5762111	-1.1105951	2.6576480
C	1.1752555	1.8444934	0.4398926
C	1.6044281	1.5154350	1.7895897
H	2.3428952	2.2596295	2.1100227
H	2.1027881	0.5398032	1.7692000
C	0.3922076	1.4931402	2.7147743
C	-0.2420725	2.6852141	3.0803048
H	0.1380944	3.6358722	2.7130372
C	-1.3589737	2.6577924	3.9147956
H	-1.8509519	3.5861860	4.1899520
C	-1.8486309	1.4388239	4.3870157
H	-2.7273008	1.4163546	5.0240916
C	-1.2175143	0.2493630	4.0215251
H	-1.5977370	-0.7021338	4.3828986
C	-0.1005706	0.2728704	3.1837568
H	0.3921267	-0.6491433	2.8895104
C	1.6623696	-4.6598257	-0.4667613
H	1.9013525	-5.6073622	-0.9672009
H	0.8457285	-4.1775613	-1.0103772
C	1.2301946	-4.9259506	0.9701535
H	0.2991315	-5.5020364	0.9511548
H	1.0446628	-3.9893118	1.5040588
H	1.9715413	-5.5047252	1.5277145
C	4.0413213	-4.3620815	0.0515094
H	4.1836454	-5.3703114	-0.3628488
H	3.8031271	-4.4655902	1.1117710
C	5.3096011	-3.5323421	-0.0958827
H	5.6536475	-3.4782991	-1.1329283
H	6.1026862	-3.9951091	0.4998168
H	5.1536621	-2.5127788	0.2697551
C	3.0637240	-3.4112960	-2.0380733
H	3.8119600	-2.6167970	-2.0716188
H	2.1215901	-2.9790390	-2.3909398
C	3.4839266	-4.5766298	-2.9341367
H	2.7340071	-5.3721123	-2.9638196
H	4.4379946	-5.0103084	-2.6187006
H	3.6114860	-4.1990406	-3.9539009

<S*S> 0.75549969

16

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Energy = -3686.145673603
C    -3.2865523    0.0546167    0.0007004
C    -1.8874384    0.4486355    2.0827413
N    -2.0691215    0.7252698    0.6052665
H    -0.9149840    0.8677783    2.3420389
C    -1.9185915   -1.0350134    2.4135445
H    -2.6689786    1.0051438    2.6047021
C    -2.0378903    2.2074906    0.2949178
H    -2.2721516    2.2879800   -0.7689989
C    -0.6874882    2.8391203    0.5995439
H    -2.8425739    2.6713321    0.8683338
H    -3.1180113   -1.0192883    0.0914526
H    -3.2613773    0.3112066   -1.0604581
C    -4.5988535    0.4699475    0.6454599
H     0.1216180    2.2920795    0.1079650
H    -0.4800006    2.8797624    1.6708462
H    -0.6988324    3.8637621    0.2166980
H    -1.1922121   -1.5974048    1.8180890
H    -2.9095905   -1.4756067    2.2754081
H    -1.6414384   -1.1507519    3.4649375
H    -4.6391641    0.1977832    1.7037112
H    -5.4082735   -0.0580120    0.1336020
H    -4.7844136    1.5428121    0.5483398
H    -1.2528709    0.3054962    0.0975924
Cl    0.1247618   -0.4985269   -1.2822670
Zn    1.4677938   -1.2556426    0.4428135
Cl    0.9946954   -3.3694238    1.0122912
Cl    1.7542825    0.3175609    2.0190150
O     3.2843328   -1.3384594   -0.5625155
C     3.3874019   -2.3210602   -1.6581056
C     3.7067394   -1.4949715   -2.8943760
H     2.4396823   -2.8600307   -1.7032376
H     4.1949000   -3.0112015   -1.3955509
C     4.5581067   -0.3552748   -2.3125558
H     2.7852071   -1.0981897   -3.3320490
H     4.2359119   -2.0799742   -3.6506688
C     3.8412933   -0.0459509   -1.0050469
H     4.6017367    0.5204612   -2.9647141
H     5.5791200   -0.7003005   -2.1194692
H     3.0048738    0.6453614   -1.1470232
H     4.4883508    0.3114837   -0.2029741
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17

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21
Energy = -1236.732012304
C     1.9119320   -1.3352256    0.4620780
C     1.4752001   -1.0502858   -0.8515767
C     1.5562666    0.3612845   -1.0480126
C     2.0320474    0.9516303    0.1498362
H     1.1336421   -1.7748568   -1.5781994
C     2.2404294   -0.1010311    1.0951724
H     1.9355255   -2.3142131    0.9251657
H     2.5847299    0.0172224    2.1156594
Ti    0.0000000    0.0000000    0.6569135
C    -2.0320474   -0.9516303    0.1498362
C    -2.2404294    0.1010311    1.0951724
C    -1.5562666   -0.3612845   -1.0480126
C    -1.4752001    1.0502858   -0.8515767
C    -1.9119320    1.3352256    0.4620780
H    -1.2907166   -0.8881311   -1.9540488
H    -2.1970917   -2.0075345    0.3207989
H    -2.5847299   -0.0172224    2.1156594
H    -1.1336421    1.7748568   -1.5781994
H    -1.9355255    2.3142131    0.9251657
H     1.2907166    0.8881311   -1.9540488
H     2.1970917    2.0075345    0.3207989
$symmetry c2
$alpha shells
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 a       1-24                                    ( 1 )
 b       1-22                                    ( 1 )
$beta shells
 a       1-23                                    ( 1 )
 b       1-22                                    ( 1 )

<S*S>     0.75658757
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18

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34
Energy = -1469.373821995
C     2.2419958   -0.7650931   -0.9950123
C     1.7100819   -0.8727631   -2.3037675
C     1.4051830    0.4401780   -2.7591170
C     1.7146925    1.3589374   -1.7208258
H     1.5644211   -1.7903896   -2.8578844
C     2.2453237    0.6069819   -0.6336461
H     2.5623206   -1.5923876   -0.3747582
H     2.5668123    1.0164447    0.3150671
Ti    0.0000000   -0.0000000   -0.9354162
C    -1.7146925   -1.3589374   -1.7208258
C    -2.2453237   -0.6069819   -0.6336461
C    -1.4051830   -0.4401780   -2.7591170
C    -1.7100819    0.8727631   -2.3037675
C    -2.2419958    0.7650931   -0.9950123
H    -0.9919899   -0.6968356   -3.7241754
H    -1.5975282   -2.4337367   -1.7599508
H    -2.5668123   -1.0164447    0.3150671
H    -1.5644211    1.7903896   -2.8578844
H    -2.5623206    1.5923876   -0.3747582
H     0.9919899    0.6968356   -3.7241754
H     1.5975282    2.4337367   -1.7599508
C     0.2492411   -0.7260536    3.4054022
C     0.8487911   -0.8681741    2.0172646
O     0.0000000    0.0000000    1.1607823
C    -0.8487911    0.8681741    2.0172646
C    -0.2492411    0.7260536    3.4054022
H     0.9948093   -0.9186578    4.1796353
H    -0.5852606   -1.4212078    3.5367477
H     0.7971133   -1.8740810    1.6005127
H     1.8684355   -0.4804448    1.9602650
H    -1.8684355    0.4804448    1.9602650
H    -0.7971133    1.8740810    1.6005127
H    -0.9948093    0.9186578    4.1796353
H     0.5852606    1.4212078    3.5367477
$symmetry c2
$alpha shells
 a       1-35                                    ( 1 )
 b       1-31                                    ( 1 )
$beta shells
 a       1-34                                    ( 1 )
 b       1-31                                    ( 1 )

<S*S>     0.75536497
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19

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37
Energy = -1600.812149193
C    -0.1465080   -2.8161709    2.4829073
C    -1.4844344   -2.6202473    2.9344596
C    -2.3512302   -3.0392473    1.8888660
C    -1.5526888   -3.4808288    0.7934592
H    -1.7864570   -2.2324755    3.8986090
C    -0.1955287   -3.3610081    1.1707178
H     0.7533516   -2.5701561    3.0330429
H     0.6579776   -3.5929506    0.5484585
Ti   -1.1405218   -1.1832712    1.1625016
C    -1.5420154    0.9323965    0.3199708
C    -1.9567270   -0.0002235   -0.6787591
C    -2.3884325    0.7716039    1.4540524
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C    -3.3120999   -0.2592188    1.1635285
C    -3.0435227   -0.7376930   -0.1527645
H    -2.3191160    1.3197883    2.3853285
H    -0.7261379    1.6375147    0.2324414
H    -1.5069428   -0.1342472   -1.6534547
H    -4.0792508   -0.6280327    1.8302090
H    -3.5705253   -1.5382344   -0.6543190
N     0.7652255   -0.7592886    0.3677566
H    -3.4315675   -3.0241203    1.9152665
H    -1.9201208   -3.8446465   -0.1567908
C     1.7785794   -0.4043703   -0.0684805
C     2.9820049    0.1471432   -0.6703778
C     2.6327142    1.4767057   -1.3330946
H     3.3678738   -0.5781410   -1.3950495
H     3.7352583    0.2706638    0.1152700
C     2.2015564    1.5026483   -2.6622435
C     2.7016344    2.6633271   -0.5978771
C     2.3482389    3.8741320   -1.1945372
C     1.9200718    3.9008225   -2.5233680
C     1.8487851    2.7146484   -3.2566583
H     2.1466027    0.5795125   -3.2335573
H     1.5213504    2.7319292   -4.2919479
H     2.4104339    4.7951668   -0.6225257
H     1.6463649    4.8437943   -2.9873144
H     3.0358037    2.6427751    0.4362740

<S*S>     0.75562999
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20

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38
Energy = -1621.922428994
C     1.7473003   -1.7713193   -1.2253395
C     2.9627329   -1.0861434   -1.5056392
C     3.5884765   -0.7546275   -0.2688890
C     2.7717367   -1.2581789    0.7736110
H     3.3446959   -0.8602730   -2.4907678
C     1.6402472   -1.8858141    0.1874563
H     1.0535708   -2.1656151   -1.9559599
H     0.8201463   -2.3425822    0.7258532
Ti    1.5497371    0.3954730   -0.3876495
C     0.1934392    1.9668310   -1.5206655
C     0.9619567    2.6526627   -0.5406952
C     1.0861313    1.4050717   -2.4643116
C     2.4104574    1.7644190   -2.0779611
C     2.3384284    2.5253560   -0.8798075
H     0.8137442    0.8108039   -3.3263963
H    -0.8840857    1.8635166   -1.5239367
H     0.5690655    3.1560646    0.3330076
H     3.3172847    1.5023575   -2.6041479
H     3.1743423    2.9478809   -0.3384452
O     0.1985739    0.4076917    1.0699832
H     4.5209139   -0.2194124   -0.1483908
H     2.9532733   -1.1424290    1.8348253
C    -0.8861791    0.2676570    1.6896118
C    -0.9553592    0.7537033    3.1025827
H     0.0079450    1.1695107    3.3968339
H    -1.2252049   -0.0696455    3.7727219
H    -1.7333486    1.5194919    3.1973644
C    -2.0293065   -0.3539362    1.0297045
C    -3.2544798   -0.4989842    1.7103135
H    -3.3582691   -0.1481961    2.7313106
C    -4.3386342   -1.0917742    1.0743234
H    -5.2812015   -1.2003521    1.6009625
C    -4.2141332   -1.5470556   -0.2415468
H    -5.0630820   -2.0101406   -0.7354281
C    -3.0013390   -1.4098888   -0.9264366
H    -2.9097753   -1.7657538   -1.9476566
C    -1.9169565   -0.8175106   -0.2962456
H    -0.9728448   -0.7088590   -0.8241494
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<S*S> 0.75498460

21

51
Energy = -1854.545872293

C	1.7633369	-1.6218520	-1.6498872
C	2.9529333	-0.8615461	-1.7351708
C	3.4946516	-0.7323572	-0.4239763
C	2.6475687	-1.4356529	0.4624246
H	3.3734131	-0.4478919	-2.6405050
C	1.5708685	-1.9750416	-0.2852156
H	1.1108679	-1.8708147	-2.4752981
H	0.7368589	-2.5371308	0.1116063
Ti	1.3827450	0.3870361	-0.4669193
C	0.4844895	2.3664264	-1.5012577
C	0.9877778	2.7348299	-0.2337136
C	1.5641194	1.8994492	-2.2910114
C	2.7489088	2.0183977	-1.5133768
C	2.3949171	2.5104833	-0.2338193
H	1.4979214	1.5317451	-3.3063015
H	-0.5501259	2.3964560	-1.8116350
H	0.4068778	3.1073797	0.5987551
H	3.7484262	1.7666897	-1.8364083
H	3.0797928	2.7168498	0.5768670
O	-0.5481982	-0.1749697	-0.6998650
H	4.3920330	-0.1918763	-0.1542792
H	2.7828900	-1.5164022	1.5327466
C	-1.7835433	0.0934981	-0.6074738
C	-2.2446741	1.3161306	0.1328781
H	-1.4048812	1.7652503	0.6622899
H	-3.0319337	1.0601644	0.8492924
H	-2.6691056	2.0549593	-0.5580367
C	-2.7405133	-0.8187707	-1.2226746
C	-4.1259093	-0.5585778	-1.1853958
H	-4.5021441	0.3308036	-0.6908687
C	-5.0215328	-1.4365676	-1.7870452
H	-6.0862887	-1.2264271	-1.7554908
C	-4.5534951	-2.5860709	-2.4300118
H	-5.2554499	-3.2702760	-2.8973532
C	-3.1799350	-2.8552156	-2.4726965
H	-2.8168440	-3.7483204	-2.9723863
C	-2.2810056	-1.9806177	-1.8785081
H	-1.2157422	-2.1792603	-1.9084280
H	-0.2626162	-0.7573709	4.4838454
H	2.1251641	-0.3718390	4.1362859
C	0.0203985	0.0355355	3.7880535
C	1.4760786	0.4920912	3.9643753
H	-0.6705171	0.8759257	3.9081286
H	1.6074268	1.1953288	4.7893361
H	0.4558954	-1.4499741	2.2555273
C	0.0178732	-0.4517024	2.3516104
H	2.8194475	0.9694935	2.2832844
C	1.7964063	1.1416563	2.6226954
O	0.8841420	0.5064323	1.6471040
H	-0.9530009	-0.4272716	1.8617455
H	1.5732260	2.2107852	2.6061580

<S*S> 0.75773048

22

47
Energy = -1702.000489182

C	2.1261982	-1.0058471	-0.9343941
C	1.4069759	-1.7073093	-1.9467241
C	1.2128898	-0.8155271	-3.0286206
C	1.8030237	0.4358458	-2.6892756
C	2.3821579	0.3059673	-1.4099848
H	2.9017640	1.0898168	-0.8767001
Ti	-0.0000000	0.0000000	-1.1689550

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C    -1.8030237   -0.4358458   -2.6892756
C    -2.3821579   -0.3059673   -1.4099848
C    -1.2128898    0.8155271   -3.0286206
C    -1.4069759    1.7073093   -1.9467241
C    -2.1261982    1.0058471   -0.9343941
H    -1.8088865   -1.3271016   -3.3023550
H     1.8088865    1.3271016   -3.3023550
C    -1.1598902   -3.2805831    1.7129916
C    -0.3976301   -2.7683559    0.4890306
O    -0.4929444   -1.2962408    0.5415751
C    -1.3871744   -0.9280760    1.6447503
C    -1.2141057   -2.0566972    2.6420702
H    -0.6563548   -4.1368851    2.1661880
H    -2.1726380   -3.5833429    1.4321180
H    -0.8267703   -3.0996695   -0.4588811
H     0.6664188   -3.0088963    0.5203854
H    -2.4137938   -0.8830773    1.2679557
H    -1.0822614    0.0596242    1.9861577
H    -2.0423776   -2.1002773    3.3541295
H    -0.2765277   -1.9411997    3.1953817
H     2.0423776    2.1002773    3.3541295
C     1.3871744    0.9280760    1.6447503
H     0.2765277    1.9411997    3.1953817
C     1.2141057    2.0566972    2.6420702
O     0.4929444    1.2962408    0.5415751
C     1.1598902    3.2805831    1.7129916
C     0.3976301    2.7683559    0.4890306
H     2.1726380    3.5833429    1.4321180
H     0.6563548    4.1368851    2.1661880
H    -0.6664188    3.0088963    0.5203854
H     0.8267703    3.0996695   -0.4588811
H     1.0822614   -0.0596242    1.9861577
H     2.4137938    0.8830773    1.2679557
H    -0.6979985    1.0436788   -3.9511267
H    -1.0899749    2.7401904   -1.9143579
H    -2.4283033    1.4044448    0.0246938
H    -2.9017640   -1.0898168   -0.8767001
H     2.4283033   -1.4044448    0.0246938
H     0.6979985   -1.0436788   -3.9511267
H     1.0899749   -2.7401904   -1.9143579
$symmetry c2
$alpha shells
 a       1-44                                   ( 1 )
 b       1-42                                   ( 1 )
$beta shells
 a       1-43                                   ( 1 )
 b       1-42                                   ( 1 )

<S*S>     0.75594401
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23 (triplet)

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76
Energy = -3683.230253291
Ti   -2.6526669   -1.0178709    0.0449761
Ti    1.8190926    0.6158138    0.4282591
N    -3.0403729    1.0670425   -0.0495901
O     2.0480721   -1.1418498   -0.5045808
C     2.0341972   -2.4150720   -0.4886338
C    -3.1467058    2.2188240    0.0188991
Cl   -0.4841843   -0.1395312    1.0990881
C    -2.1110585   -0.5333116   -2.2178623
C    -1.1169176   -1.4233132   -1.7511016
C    -3.3673072   -1.2054883   -2.1741887
C    -3.1300607   -2.5173404   -1.6892637
C    -1.7397776   -2.6455134   -1.4034451
H    -3.8763156   -3.2865428   -1.5525886
H    -1.2484226   -3.5229980   -1.0055459
H    -1.9525294    0.4866028   -2.5380335
H    -4.3231453   -0.7943809   -2.4698820
C    -3.5174007   -2.8659852    1.2593337
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C    -4.6309304   -2.0668241    0.8654366
C    -4.5188100   -0.8146476    1.5069191
C    -3.3248990   -0.8225055    2.2802148
C    -2.7141287   -2.1019242    2.1350432
H    -2.9402166    0.0002675    2.8660879
H    -1.7860183   -2.4191282    2.5893475
H    -3.3143236   -3.8760162    0.9304389
H    -5.4180493   -2.3625014    0.1854398
H    -5.2003760    0.0174057    1.3956940
C     2.2898549   -0.3526847    2.5422182
C     3.5105417   -0.3296774    1.8253437
C     3.8529678    1.0218538    1.5859061
C     2.8553918    1.8401117    2.1946664
C     1.8869014    0.9946494    2.7722461
H     2.8305045    2.9206949    2.1901290
H     0.9850957    1.3072390    3.2779020
H     1.7478478   -1.2306738    2.8582325
H     4.0648698   -1.1894801    1.4743362
H     4.7218790    1.3699555    1.0443238
C     2.5760932    2.6104430   -0.5968886
C     1.2080515    2.8021422   -0.2660524
C     0.4448008    1.9189624   -1.0700475
C     1.3334701    1.1712732   -1.8731092
C     2.6594799    1.5812284   -1.5702333
H     1.0579864    0.3941880   -2.5709342
H     3.5679945    1.1900593   -2.0082921
H     3.4122406    3.1492175   -0.1757200
H     0.8163086    3.4940006    0.4660354
H    -0.6268520    1.8005867   -1.0325718
C     1.6176345   -3.1393308    0.7564681
C     2.4229816   -3.1154569   -1.7054118
H     0.8804493   -2.5323679    1.2856435
H     2.4831825   -3.2896716    1.4153836
H     1.1947849   -4.1214496    0.5401674
H    -0.0726041   -1.1903550   -1.6186652
C    -3.1905459    3.6637626    0.1742421
C     2.4295952   -4.5244509   -1.7870805
C     2.8090104   -2.3707944   -2.8427837
C     2.7998443   -5.1608138   -2.9671996
C     3.1727922   -3.0116502   -4.0183315
H     2.8200768   -1.2886321   -2.7801411
H     2.1480334   -5.1246370   -0.9287936
C     3.1687617   -4.4103717   -4.0872667
H     2.8001478   -6.2456553   -3.0156375
H     3.4641939   -2.4260831   -4.8853715
H     3.4545890   -4.9108682   -5.0076549
C    -2.0134267    4.1726412    1.0022703
H    -4.1458578    3.9247910    0.6489273
H    -3.1917187    4.1191153   -0.8215966
C    -1.3752276    5.3589243    0.6309075
C    -1.5840023    3.4828387    2.1400220
C    -0.5338492    3.9842027    2.9080146
C     0.0995303    5.1732651    2.5403695
C    -0.3222037    5.8586288    1.3995359
H     0.1707435    6.7794066    1.1020699
H    -1.6981229    5.8913558   -0.2597794
H    -2.0606158    2.5484460    2.4223877
H    -0.2102649    3.4469030    3.7942836
H     0.9199153    5.5610068    3.1370686

<S*S>     2.01391245
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24

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54
Energy = -1985.990096066
C     1.7571372   -3.0607850   -0.3357617
C     3.1261635   -2.9892281   -0.6879013
C     3.8209687   -2.3212745    0.3611264
C     2.8807120   -1.9881229    1.3606254
H     3.5659489   -3.3706843   -1.5990059
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C     1.6005721   -2.4301317    0.9286357
H     0.9703020   -3.4875361   -0.9424966
H     0.6697552   -2.2874853    1.4600448
Ti    2.2787069   -0.7739344   -0.6100499
C     2.1745490    0.4662359   -2.6642199
C     2.8090873    1.2774453   -1.6963655
C     2.9741374   -0.6845635   -2.8721301
C     4.1327380   -0.5598214   -2.0530759
C     4.0230385    0.6374143   -1.3058811
H     2.7516376   -1.5016047   -3.5454545
H     1.2223619    0.6611300   -3.1372044
H     2.4430197    2.2176178   -1.3083804
H     4.9466684   -1.2680775   -1.9989661
H     4.7348539    1.0079824   -0.5805906
O     0.2474032   -0.6630326   -0.8248278
N     1.9003620    0.6286477    0.9385229
H     4.8782952   -2.0957182    0.3840319
H     3.0935655   -1.4566854    2.2777091
C    -0.8060616    0.0132180   -0.9833187
C    -0.7482331    1.4924535   -1.2279705
H     0.2594272    1.8613576   -1.0463005
H    -1.4509682    2.0169982   -0.5737133
H    -1.0315137    1.7211321   -2.2630109
C    -2.0943519   -0.6750002   -0.9090244
C    -3.2992249    0.0033311   -1.1761014
H    -3.2854192    1.0497986   -1.4606345
C    -4.5166646   -0.6615725   -1.0746822
H    -5.4405313   -0.1310959   -1.2843391
C    -4.5517570   -2.0070820   -0.6986377
H    -5.5040723   -2.5221298   -0.6134307
C    -3.3599723   -2.6918161   -0.4327115
H    -3.3874137   -3.7372900   -0.1404973
C    -2.1419353   -2.0346934   -0.5422132
H    -1.2138506   -2.5557326   -0.3362889
C     1.4768518    1.3297582    1.7570951
C     0.8008892    2.1686022    2.7357015
C    -0.6903178    2.2017381    2.4113005
H     1.2368123    3.1718607    2.7032734
H     0.9904602    1.7537221    3.7329448
C    -1.4421971    1.0220730    2.4523792
C    -2.7959973    1.0436559    2.1243701
H    -0.9681308    0.0853376    2.7347462
C    -3.4058868    2.2440459    1.7514362
C    -2.6580436    3.4215752    1.7122058
C    -1.2994236    3.4009040    2.0378950
H    -0.7151184    4.3162363    1.9975532
H    -3.1277320    4.3571198    1.4233225
H    -3.3720279    0.1239322    2.1505801
H    -4.4595799    2.2597739    1.4896870

<S*S>     0.75686668
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25

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50
Energy = -1833.445547855
C    -1.5117686   -2.7034194   -0.1426825
C    -2.8195866   -2.2852858    0.2345373
C    -3.5402426   -2.0077095   -0.9560989
C    -2.6779042   -2.2376965   -2.0646636
H    -3.2079948   -2.2162586    1.2413280
C    -1.4351102   -2.6856987   -1.5566438
H    -0.7046848   -2.9576742    0.5307883
H    -0.5623827   -2.9286939   -2.1463466
Ti   -1.7979736   -0.4345389   -0.7859696
C    -2.4257750    1.7922336   -0.1123023
C    -1.5746440    1.8787301   -1.2400006
C    -3.5974330    1.0991104   -0.4919517
C    -3.4874688    0.7887909   -1.8805208
C    -2.2369885    1.2593749   -2.3434107
H    -4.4333076    0.8571214    0.1510898
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H    -2.1976071    2.1535858    0.8811188
H    -0.5947250    2.3351230   -1.2637920
H    -4.2280650    0.2725130   -2.4744867
H    -1.8510685    1.1669887   -3.3496097
N     0.1418815   -0.3683168   -1.6281288
H    -4.5676652   -1.6764952   -1.0083742
H    -2.9262449   -2.0969253   -3.1081176
C     1.2221365   -0.2889324   -2.0429278
C     2.6294196   -0.1398237   -2.3899739
C     3.3846364    0.2481821   -1.1221791
H     2.7192287    0.6265500   -3.1671149
H     2.9925866   -1.0860600   -2.8039487
C     3.4524758    1.5889971   -0.7319914
C     3.9409127   -0.7423895   -0.3076748
C     4.5640257   -0.3922165    0.8911351
C     4.6277983    0.9466662    1.2818377
C     4.0750139    1.9369395    0.4669403
H     3.0176948    2.3600270   -1.3630789
H     4.1276991    2.9802110    0.7639885
H     4.9982900   -1.1649936    1.5184799
H     5.1098155    1.2180281    2.2163762
H     3.8857063   -1.7854824   -0.6084860
H     1.3296430   -0.2050355    0.7840368
H     1.2298355   -0.3318014    3.1787561
C     0.5943171    0.4406010    1.2622569
C     0.7806302    0.5769434    2.7662992
H     1.4208586    1.4260622    3.0147383
H     0.5632819    1.4082190    0.7533718
O    -0.7238208   -0.1927680    1.0946977
H    -1.3744563   -1.2581391    2.7593230
C    -0.6602509    0.7420956    3.2717958
C    -1.4242630   -0.2299497    2.3872598
H    -0.7725929    0.5001816    4.3309283
H    -1.0103168    1.7664922    3.1074860
H    -2.4635462    0.0465365    2.2019059

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26

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92
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Ti    2.9011135   -2.2456825    1.0092831
N    -1.5590871   -0.4084393    0.2954822
O     1.5231791   -1.5073892    0.0278821
C     0.3835454   -1.5057343   -0.7913330
C    -0.4414907   -0.2875978   -0.2604698
C     0.2263387    1.0738641   -0.4182399
N    -3.1388689    1.6845035    1.3913384
C    -0.3951115   -2.8150554   -0.6613095
H     0.1853796   -3.6332757   -1.0905143
H    -1.3459558   -2.7503626   -1.1936558
H    -0.5918677   -3.0270089    0.3904929
C    -1.7930009   -1.6135202    2.7289541
C    -1.8982772   -0.2768557    3.1845914
C    -3.0833969   -2.1960928    2.7823422
C    -3.9826335   -1.2276094    3.3206180
C    -3.2526894   -0.0460006    3.5648651
H    -5.0414319   -1.3656606    3.4898914
H    -3.6593537    0.8809010    3.9446131
H    -1.0921882    0.4421421    3.2277051
H    -0.8858813   -2.0900355    2.3851242
H    -3.3362782   -3.2050098    2.4863775
C    -5.0953881   -1.7025028    0.5802550
C    -4.1266838   -1.8399726   -0.4443860
C    -3.9525323   -0.5656282   -1.0542307
C    -4.7994318    0.3519662   -0.3967396
C    -5.4920941   -0.3388303    0.6343182
H    -4.8822521    1.4076005   -0.6131314
H    -6.2034262    0.0934066    1.3251709
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H    -5.4567991   -2.4953424    1.2191663
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C     2.6344578   -4.4946235    0.1909096
C     2.9790511   -3.6974289   -0.9153801
C     4.2732284   -3.1599090   -0.6886569
C     4.7595278   -3.7041108    0.5364863
C     3.7422161   -4.4997235    1.0927241
H     5.7266040   -3.5079085    0.9759227
H     3.7770704   -5.0041175    2.0478604
H     1.6881332   -4.9877848    0.3561585
H     2.3478190   -3.4646493   -1.7603086
H     4.8138889   -2.4986091   -1.3520927
C     3.7082000    0.0263627    0.9093021
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C     4.6558612   -1.4048791    2.4350181
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H     3.0262621   -1.1918667    3.9345118
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H     3.5271528    0.5838247    0.0007364
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H     5.3279157   -2.1045061    2.9117787
Cl    1.4745815   -3.1577245    2.7143619
H     1.7267169    2.0741061   -2.4552560
C     0.6706002    2.2885540   -2.5892046
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H    -2.3249155    1.7539540   -1.1005256
C    -2.0392291    2.8262101   -2.9456065
H    -3.0980203    3.0328504   -3.0788001
C    -1.1133724    3.2792568   -3.8883743
H    -1.4471826    3.8369252   -4.7588737
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H     0.9713285    3.3534061   -4.4340583
C     2.0527911   -0.8778171   -2.6156478
C     2.3550333   -0.5525324   -3.9389721
H     3.3782075   -0.3108254   -4.2133557
C     1.3465419   -0.5236698   -4.9014099
H     1.5783906   -0.2595867   -5.9290853
C     0.0337709   -0.8290938   -4.5344651
H    -0.7605863   -0.7992507   -5.2746085
C    -0.2633520   -1.1653989   -3.2163457
H    -1.2897175   -1.3903222   -2.9415315
C     0.7450745   -1.1965246   -2.2439699
H     1.3056892    0.9206684   -0.4792208
H     0.0136756    1.6583311    0.4822984
H     2.8325236   -0.8826967   -1.8620616
C    -2.8554448    2.8047419    1.4417649
C    -2.3407273    4.1652871    1.5027350
C    -0.8153920    4.1052037    1.4985178
H    -2.7283726    4.6432034    2.4096537
H    -2.7204166    4.7217795    0.6401557
C    -0.1347222    3.5778398    2.6025004
C    -0.0996429    4.5279809    0.3775884
C     1.2927928    4.4255194    0.3604078
C     1.9704712    3.8933811    1.4569925
C     1.2549062    3.4729488    2.5814981
H    -0.6906529    3.2493530    3.4773166
H     1.7783540    3.0626114    3.4398208
H     3.0525360    3.8039493    1.4376068
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H    -0.6267278    4.9204341   -0.4871004
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92
Energy = -4047.301747802
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Ti    3.1848019    0.0620889   -1.2563275
N    -2.0786872   -0.4178747   -0.2114621
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C	-0.2533959	0.2445405	1.2403198
Cl	-4.1987904	-1.6072658	-2.4059915
C	-0.1287315	-1.5215023	-1.9984319
H	0.3382821	-1.5886269	-2.9811177
H	-1.1941964	-1.7436340	-2.0959453
H	0.3220516	-2.2608242	-1.3294270
C	-4.0093169	1.2456234	0.8552573
C	-4.1242515	1.3971581	-0.5580837
C	-5.1383322	0.5285562	1.3073675
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C	-5.3307017	0.7850600	-0.9657708
H	-6.8804110	-0.3302217	0.1860993
H	-5.6851010	0.7020085	-1.9815436
H	-3.4038179	1.8693247	-1.2102234
H	-3.1931906	1.6011418	1.4679771
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C	-2.7435918	-2.5755385	1.2400357
C	-3.2665201	-3.2323240	0.1037959
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H	-6.0365479	-2.2605165	1.6965477
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C	4.4643722	-1.2494477	-2.7957420
H	5.7382576	0.5624327	-2.9791261
H	5.1516474	-1.9945483	-2.4176906
H	2.5430890	-2.3859868	-2.9597028
H	1.5193069	-0.0393400	-3.8151018
H	3.4728043	1.7831428	-3.7695540
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C	5.1669690	1.2133793	-0.4443981
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C	3.3752804	0.9612054	0.9670793
C	3.0872999	2.0355441	0.1047247
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H	2.1705568	2.6081763	0.0942929
H	4.2587650	2.9111154	-1.5873379
H	6.1299459	1.0816437	-0.9136231
H	5.1725532	-0.3712247	1.1075365
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C	0.6353952	2.1293669	2.6542264
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C	-0.5730494	2.7090448	0.6553174
H	-1.1264264	2.4179110	-0.2310404
C	-0.3619412	4.0643737	0.9194739
H	-0.7555470	4.8120321	0.2364948
C	0.3526571	4.4548137	2.0516770
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H	1.3960681	3.7731506	3.8137876
C	0.3085899	2.1538262	-2.5342621
C	-0.1422948	3.1557563	-3.3934869
H	0.4469376	4.0598669	-3.5197145
C	-1.3462602	2.9999814	-4.0817459
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H	-3.0339541	1.7003145	-4.4259216
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H     0.7165805   -0.2588978    1.3170550
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H     2.1399636   -4.4560701    1.0874241
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C     2.5279234   -1.9350494    3.4050070
C     1.8016000   -1.2795272    4.3978037
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C    -0.1249125   -2.6473840    3.8924769
H    -1.1548476   -2.9328272    4.0846416
H     0.1325287   -4.0901276    2.3083364
H    -0.0937875   -1.1226514    5.4144028
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H     3.5646110   -1.6625980    3.2232112
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76
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N    -1.3039132   -0.5308766   -0.3114712
O     0.9942385   -0.2706945    0.9414923
C     1.1211791   -0.7478978   -0.3765105
C    -0.3164392   -1.0035787   -0.9259639
Cl   -1.4473889    0.9742843    2.5898307
C    -2.4409669    2.3809022   -0.0012391
C    -2.5994465    1.6643507   -1.2058388
C    -3.6667460    2.3078424    0.7215366
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C    -3.9107787    1.1232165   -1.2295465
H    -5.6018809    1.3290668    0.2136721
H    -1.5440765    2.8790547    0.3348857
H    -3.8596672    2.7432525    1.6926088
C    -3.4308060   -2.1666436    0.3364980
C    -4.6180323   -1.4014259    0.4003907
C    -4.7080987   -0.8360602    1.7087719
C    -3.5746393   -1.2505662    2.4376293
C    -2.7697101   -2.0546895    1.5893143
H    -3.3486080   -0.9632214    3.4538892
H    -3.0754271   -2.7149763   -0.5237222
H    -5.3378085   -1.2774369   -0.3963023
C    -0.1592569   -1.4538605    3.9706359
C     0.6271277   -2.1249305    3.0146700
C     1.9873715   -1.8104422    3.2661273
C     2.0359418   -0.9807400    4.4169935
C     0.7084056   -0.7304444    4.8364835
H     2.9339596   -0.5978937    4.8788258
H     0.4025499   -0.1101707    5.6677493
H    -1.2356667   -1.4647315    4.0351843
H     0.2631532   -2.7195760    2.1905456
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C     1.2625505    2.5675843    2.0357549
C     2.4839316    1.9149036    1.7926601
H     2.9220638    1.7261463    0.8237105
H     3.9004163    0.8894604    3.1799117
H     2.2049013    1.7070757    5.1213061
H     0.1613956    2.9708041    3.9457928
C     1.9393099   -2.0409286   -0.3620621
C     1.7329849    0.3701911   -1.2265069
H     2.0852460   -2.4256272   -1.3732539
H     1.4249249   -2.8009859    0.2294860
H     2.9184158   -1.8454547    0.0825819
H    -1.8421418    1.5176737   -1.9606781
C    -0.4863565   -1.8367427   -2.1979014
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C     2.9120834    0.2193901   -1.9575177
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C     1.5778046    2.6741007   -1.9739985
C     2.7570944    2.5174186   -2.7077445
C     0.3391916   -1.3993056   -3.3889935
H    -1.5523885   -1.8092534   -2.4420166
H    -0.2341633   -2.8740447   -1.9445969
C     0.1148919   -0.1544292   -3.9903880
C     1.3345807   -2.2295067   -3.9136354
C     2.1093889   -1.8162723   -4.9993737
C     1.8931986   -0.5646338   -5.5746176
C     0.8878725    0.2642686   -5.0696037
H     0.7111505    1.2394422   -5.5137841
H    -0.6609892    0.4987815   -3.6012094
H     1.5052638   -3.2080785   -3.4706387
H     2.8808536   -2.4724391   -5.3926579
H     2.5007621   -0.2362087   -6.4129626
H     2.8391618   -2.1498418    2.6926485
H     0.6076404    2.9920683    1.2901549
H    -5.5017129   -0.2020052    2.0783036
H    -1.8240316   -2.5059164    1.8432013
H    -4.3299228    0.5090957   -2.0147952
H     0.1608018    1.7080513   -0.6657919
H     1.0546026    3.6263562   -1.9771925
H     3.1535201    3.3458372   -3.2876321
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TS-30

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79
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C     0.6106598   -2.2262683    5.5967441
C    -0.2906619   -1.2123808    5.9630402
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H     0.4747786   -3.2864852    5.7512031
H    -1.2550732   -1.3505238    6.4319682
C     0.2142601   -2.7506781    1.7441152
C    -1.0981937   -2.2559398    1.5484250
C    -1.8922428   -2.6924636    2.6373797
C    -1.0749368   -3.4387087    3.5137419
C     0.2384380   -3.4743138    2.9596416
H     1.0651958   -2.5702596    1.1038935
H    -1.4287683   -1.6361363    0.7278895
H    -2.9338510   -2.4556467    2.7934066
H    -1.3921343   -3.8951329    4.4405922
H     1.0981908   -3.9732386    3.3834717
Ti    0.0556189   -1.0957397   -3.7208488
Cl   -2.0268722   -0.9321774   -2.4494967
C    -0.0823889    0.9396953   -5.0548756
C     0.6682225   -0.0191690   -5.8005443
C    -0.1902367   -1.0863910   -6.1210694
C    -1.4538521   -0.8333405   -5.5214293
C    -1.3891651    0.4512635   -4.9077437
H     0.3075893    1.8608070   -4.6491946
H     0.0796643   -1.9513625   -6.7074700
H    -2.3177344   -1.4823234   -5.5464843
H    -2.1861671    0.9301676   -4.3615478
C     1.4141965   -2.9378341   -4.2558235
C     1.5635324   -2.7569515   -2.8554427
C     0.3175308   -3.0018519   -2.2441965
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H	2.1829768	-2.7946756	-5.0021950
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H	-1.6477061	-3.6093386	-3.1122074
H	-0.3564190	-3.6287540	-5.4454347
H	1.7127609	0.0578892	-6.0610113
N	0.6252284	-0.3048772	-0.9028201
C	0.2996388	0.3839717	0.1210783
C	1.2320780	0.6327600	1.3307493
C	2.6430350	0.0660202	1.1386461
H	2.6090339	-1.0160322	0.9822355
H	3.2288422	0.2671249	2.0384194
H	3.1436106	0.5344602	0.2865321
O	0.6291419	-0.0202706	2.4244534
C	1.2839865	2.1375016	1.5997716
C	1.8883997	2.9879069	0.6651814
C	0.6785184	2.6856748	2.7317715
C	1.8936276	4.3659565	0.8665052
H	2.3297121	2.5767521	-0.2387670
C	0.6911523	4.0667086	2.9371972
H	0.1773790	2.0276534	3.4329191
C	1.2973905	4.9101451	2.0066323
H	2.3516398	5.0163509	0.1268292
H	0.2125918	4.4832959	3.8196475
H	1.2956097	5.9856735	2.1603033
C	-1.1208502	2.3846967	-0.4212510
C	-0.6162574	2.5900456	-1.7107503
C	-1.6844466	3.4651353	0.2640192
C	-1.7420930	4.7288468	-0.3248201
H	-2.0622995	3.3178226	1.2721423
C	-0.6729011	3.8512248	-2.3013662
H	-0.1560252	1.7577336	-2.2344275
C	-1.2359579	4.9271777	-1.6103728
H	-2.1735557	5.5608040	0.2255613
H	-0.2711891	4.0005777	-3.3007166
H	-1.2743049	5.9121311	-2.0678919
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H	-1.3633731	1.0798646	1.2729008
H	-1.7752487	0.3529630	-0.3006161
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Cl	2.1728652	0.1156369	-3.2888419

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56

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Ti	2.5589044	-0.6359687	1.0291166
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C	-1.5789342	-0.2744414	1.5966741
C	-3.0409699	-0.2933367	1.2068640
C	-0.7157032	-2.5346529	0.9883621
H	-0.0764151	-3.1186100	0.3215332
H	-1.7488512	-2.8746119	0.8744707
H	-0.3964243	-2.7076331	2.0181501
C	3.0658751	-2.6196636	-0.2625994
C	2.1456153	-1.8749947	-1.0182636
C	2.7431016	-0.6270918	-1.3443778
C	4.0721109	-0.6433972	-0.8461577
C	4.2612462	-1.8496022	-0.1371588
H	4.7958505	0.1499545	-0.9585402
H	5.1485866	-2.1396119	0.4091725
H	2.8888026	-3.5854505	0.1858869
H	1.1366409	-2.1646697	-1.2668872
H	2.2733089	0.1757958	-1.8958630
C	3.2602245	1.6376437	0.8637870
C	4.3126546	0.9553492	1.5492200
C	3.8066554	0.5164280	2.7854331
C	2.4510455	0.9411864	2.8885412
C	2.1296317	1.6575082	1.7172591
H	1.7863922	0.7188328	3.7121460

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H     1.1629625    2.0742538    1.4716382
H     3.3250455    2.0923320   -0.1151938
H     5.3130189    0.7836172    1.1791807
H     4.3408693   -0.0715752    3.5168244
Cl    2.7603284   -2.3237780    2.7253636
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C    -4.0439109    0.6393463   -0.9267958
H    -4.2843341   -0.3793408   -1.2189291
C    -4.3540288    1.6986109   -1.7801418
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C    -4.0239493    3.0061688   -1.4218189
H    -4.2579793    3.8318062   -2.0883887
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H    -3.1291951    4.2615888    0.0872218
C    -0.5239019    0.6356540   -1.2000821
C    -0.7795754    1.0349849   -2.5074161
H    -0.5348226    2.0456680   -2.8212609
C    -1.3629567    0.1418469   -3.4105767
H    -1.5675460    0.4531954   -4.4310146
C    -1.6879222   -1.1470551   -2.9923846
H    -2.1444903   -1.8475597   -3.6862639
C    -1.4336112   -1.5445032   -1.6769652
H    -1.6976605   -2.5503865   -1.3658861
C    -0.8458843   -0.6585272   -0.7708567
H    -3.6316053   -0.2356767    2.1274934
H    -3.2908534   -1.2292756    0.6979825
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TS-31

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C    -0.4002972   -1.2173846   -0.5455690
C    -1.4264184   -1.2929634    0.6033934
C    -2.7942049   -1.9527471    0.3703376
Cl    2.5962007    1.2308902    0.9079200
C     0.0247359   -2.6824148   -0.7618861
H     0.7317001   -2.7748533   -1.5848112
H    -0.8428839   -3.3181868   -0.9671483
H     0.4848280   -3.0346583    0.1658984
C     0.5351575   -1.0342425    4.1268432
C     0.6926832   -2.0063602    3.1072598
C     1.7220578   -0.2498296    4.1648967
C     2.5833363   -0.7193383    3.1564951
C     1.9389034   -1.7944557    2.4849982
H     3.5517245   -0.3011408    2.9294135
H     2.3215681   -2.3459648    1.6410432
H    -0.0456950   -2.7385368    2.8205464
H    -0.3338214   -0.9163351    4.7587965
H     1.9351984    0.5662127    4.8397120
C     0.6384002    2.5186307    2.7971697
C    -0.2051924    1.8822862    3.7388422
C    -1.3707128    1.4562923    3.0686237
C    -1.2762326    1.8650029    1.7122597
C    -0.0418636    2.5198225    1.5458095
H    -2.0068538    1.6529059    0.9453198
H     0.3444738    2.9358101    0.6297280
H     1.6180526    2.9319332    2.9907307
H     0.0111682    1.7267883    4.7856494
H    -2.1721138    0.8683806    3.4894437
C     1.6563350    1.7469502   -3.0027669
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H	0.7116167	1.4671416	-3.4400174
H	1.0442538	2.7925257	-1.1514682
H	3.6915438	3.0154850	-0.6896995
C	4.8960209	-0.2110841	-0.8071457
C	4.8067659	-0.7021745	-2.1427389
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H	3.6694186	-2.3970240	-3.0014806
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H	-3.9207254	-1.3144909	2.7615527
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H	-4.0505638	-0.3070882	-1.4071035
C	-5.3356913	0.8492914	-0.1213248
H	-5.7225829	1.4574218	-0.9350712
C	-5.7695304	1.0728601	1.1874192
H	-6.4970942	1.8522524	1.3977710
C	-5.2630124	0.2851201	2.2240915
H	-5.5960777	0.4505332	3.2456426
C	-1.2631965	0.8403503	-1.6907447
C	-2.0152268	1.5048323	-2.6575850
H	-2.1032873	2.5879537	-2.6236798
C	-2.6556075	0.7814099	-3.6657455
H	-3.2431944	1.2937514	-4.4226026
C	-2.5336699	-0.6104661	-3.6893570
H	-3.0234732	-1.1859487	-4.4707860
C	-1.7831020	-1.2694801	-2.7158286
H	-1.6864822	-2.3498235	-2.7627111
C	-1.1286366	-0.5515624	-1.7068748
H	-2.8822715	-2.8019086	1.0567256
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H	-0.7497178	1.3902272	-0.9118841

31

54

Energy = -1986.136502430

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O	1.5902115	-0.7039997	0.3253159
C	0.4501888	-1.2827557	-0.2723031
C	-0.7523981	-0.7525029	0.5896436
C	-2.1871567	-1.0612138	0.1994356
C	0.5183835	-2.8189766	-0.1458295
H	1.4311186	-3.1765722	-0.6316451
H	-0.3400473	-3.3014925	-0.6212390
H	0.5370680	-3.1042105	0.9089540
C	1.0558331	-1.7131583	3.3520879
C	2.3444093	-1.8705653	2.8047594
C	3.1688727	-0.8284319	3.3078253
C	2.3909092	-0.0587472	4.2165694
C	1.0813459	-0.5821240	4.2219405
H	2.7337414	0.8060501	4.7663294
H	0.2363189	-0.1846960	4.7687838
H	0.1865025	-2.3149344	3.1318712
H	2.6386495	-2.6019306	2.0662794
H	4.2083151	-0.6598226	3.0567696
C	2.8678673	2.1807001	2.1996321
C	1.6260166	2.4938107	2.8168940
C	0.6325749	2.5124606	1.8061463
C	1.2534715	2.2183143	0.5694756
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H	0.7514998	2.1030407	-0.3800409

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H    -0.4244473    2.6763836    1.9638481
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C    -2.3585320    1.2500224   -0.8558605
C    -2.7794169   -0.0821784   -0.8024427
C    -3.7764518   -0.5072079   -1.6886063
H    -4.1061476   -1.5437096   -1.6639006
C    -4.3343915    0.3757358   -2.6126171
H    -5.1027783    0.0263873   -3.2974026
C    -3.8988193    1.7017233   -2.6662667
H    -4.3248904    2.3888776   -3.3920993
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H    -2.5607549    3.1645658   -1.8178836
C     1.1993772    0.1282628   -2.2410487
C     1.0899942    0.5656195   -3.5616559
H     1.7620327    1.3365873   -3.9302211
C     0.1238719    0.0169658   -4.4060156
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C    -0.7155093   -0.9874415   -3.9211696
H    -1.4685598   -1.4291472   -4.5680460
C    -0.5975045   -1.4273074   -2.6040773
H    -1.2628914   -2.2093546   -2.2526197
C     0.3478021   -0.8612529   -1.7375653
H    -2.7822604   -1.0404614    1.1200598
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32

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C     0.5466815    0.6977585    5.0120895
C     1.5708708   -0.2154120    4.6788622
C     1.2134812   -1.4856543    5.1926904
C    -0.0244893   -1.3424226    5.8906103
H    -1.3494207    0.4192898    6.1571380
H     0.4922969    1.7326698    4.7064273
H     2.4403999   -0.0008208    4.0747969
H     1.7905403   -2.3947676    5.0961348
H    -0.5649809   -2.1239776    6.4048665
C    -0.6492778   -2.5697516    1.7206854
C    -1.9346426   -2.3431989    2.2388109
C    -1.9544856   -2.8135016    3.5875407
C    -0.6813826   -3.3415778    3.8794708
C     0.1526390   -3.1401643    2.7450547
H    -0.3038793   -2.2834166    0.7386083
H    -2.7553784   -1.8616133    1.7291915
H    -2.7969823   -2.7612123    4.2634060
H    -0.3752939   -3.7890893    4.8131294
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Cl   -2.3591968   -1.5219386   -2.5627023
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H	2.9652069	-0.3395533	1.8455729
H	2.9776759	-0.3586750	0.0702832
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C	1.3814382	1.7918322	0.9963289
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C	2.5101548	3.7087277	0.0424671
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C	0.8198323	4.0264255	1.7386439
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H	-1.4545622	0.5787854	1.0685264
H	-1.8911434	-0.5087955	-0.2440807
H	1.6476061	-0.4718372	-1.3757999
Cl	3.6862457	-0.1643217	-2.2806097

TS-33

79

Energy = -4604.551781471

Ti	-0.0046829	-1.1545333	3.3838557
Cl	-2.0381743	0.1055083	3.6444820
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C	1.0440639	0.3926167	4.9355834
C	2.0467281	-0.4813730	4.4595917
C	1.7290555	-1.7929039	4.8891531
C	0.5364129	-1.7203331	5.6703817
H	-0.7747103	0.0020408	6.1677153
H	0.9657771	1.4482783	4.7188870
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H	2.3023711	-2.6853253	4.6809820
H	0.0308678	-2.5475800	6.1476421
C	-0.2947729	-2.5924614	1.4353971
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C	-0.1909546	-3.5530141	3.5175340
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H	-0.0308001	-2.2259892	0.4547148
H	-2.4123092	-1.9576907	1.6090135
H	-2.2961207	-3.0739505	4.0604896
H	0.1758107	-4.0717451	4.3905878
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Ti	-0.0786482	-1.0432688	-3.2932857
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H     2.3991842   -1.2637011   -5.0532140
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H     0.8049812   -3.4982774   -1.6854992
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C     0.1884986    0.2453287   -0.2295558
C     1.2219150    0.4718816    0.9043701
C     2.5545317   -0.2396427    0.6372086
H     2.3914442   -1.3170324    0.5435827
H     3.2212196   -0.0561059    1.4815291
H     3.0486262    0.1323163   -0.2662344
O     0.6691671   -0.0647588    2.0789449
C     1.4038949    1.9837932    1.0726650
C     2.2584526    2.7018362    0.2285862
C     0.6468121    2.6676817    2.0285856
C     2.3653957    4.0867388    0.3540890
H     2.8130471    2.1946724   -0.5554672
C     0.7519424    4.0522676    2.1487420
H    -0.0383853    2.1097350    2.6582261
C     1.6140375    4.7659036    1.3144497
H     3.0286460    4.6356417   -0.3087013
H     0.1511741    4.5749381    2.8878699
H     1.6919465    5.8458281    1.4046017
C    -1.5379313    2.1024075   -0.2352229
C    -0.7727577    2.8807363   -1.1076363
C    -2.6406601    2.6847096    0.4015221
C    -2.9728067    4.0183533    0.1661313
H    -3.2297888    2.0911608    1.0963289
C    -1.0980813    4.2170366   -1.3381268
H     0.1007270    2.4504111   -1.5885362
C    -2.2009249    4.7909173   -0.7050681
H    -3.8295399    4.4571295    0.6708403
H    -0.4807929    4.8115187   -2.0060584
H    -2.4523460    5.8332354   -0.8808129
C    -1.2313932    0.6360799    0.0392582
H    -1.4639927    0.4284767    1.0881828
H    -1.8728616    0.0001414   -0.5798272
H     1.5758164   -0.3695713   -1.3966692
Cl    2.3807419    0.8759171   -3.2545239
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79
Energy = -4604.552627308
Ti   -0.1387678   -1.4605688    3.3753792
Cl   -2.1013913   -0.0969622    3.6690748
C     0.0457135   -0.7174749    5.6923427
C     0.9918919    0.0221534    4.9331476
C     1.9527775   -0.8846427    4.4340540
C     1.5869212   -2.1885967    4.8486690
C     0.4088762   -2.0781709    5.6478946
H    -0.8260446   -0.3119620    6.1836576
H     0.9535502    1.0829676    4.7312755
H     2.7845121   -0.6377563    3.7901914
H     2.1211471   -3.1006215    4.6216298
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C	0.3190130	-3.5470751	2.3299555
H	-0.2680506	-2.5066027	0.4350096
H	-2.6110344	-2.1237718	1.6352132
H	-2.5137892	-3.2661876	4.0747584
H	-0.0905585	-4.3915623	4.3565884
H	1.3481871	-3.8311178	2.1543230
Ti	-0.1422192	-0.8885083	-3.4932476
Cl	-1.6191704	-2.3511897	-1.9778020
C	-2.0706003	0.5759794	-3.3699224
C	-1.0866388	1.2380374	-4.1305434
C	-0.8307728	0.4676499	-5.2946070
C	-1.7343766	-0.6351758	-5.2866279
C	-2.4835268	-0.5758450	-4.0986377
H	-2.4600695	0.9026320	-2.4181136
H	-0.1028924	0.6974918	-6.0597670
H	-1.8372889	-1.3894681	-6.0521172
H	-3.2255140	-1.2912771	-3.7838947
C	1.7157035	-1.5640755	-4.8813569
C	1.9895659	-2.0289437	-3.5619409
C	1.0135260	-2.9809208	-3.2208007
C	0.1171287	-3.1049106	-4.3225778
C	0.5890497	-2.2635047	-5.3591095
H	2.2712229	-0.8073792	-5.4128050
H	2.7938924	-1.6749101	-2.9323661
H	0.9128789	-3.4838110	-2.2709487
H	-0.7608949	-3.7323143	-4.3562347
H	0.1542774	-2.1540573	-6.3409125
H	-0.5697466	2.1399649	-3.8489411
N	0.4936557	-0.4396433	-1.4045801
C	0.1266574	-0.0131092	-0.2515971
C	1.1524793	0.1228909	0.9023819
C	2.4502093	-0.6501151	0.6329724
H	2.2307976	-1.7117140	0.4887048
H	3.1055573	-0.5384728	1.4983074
H	2.9911168	-0.2703271	-0.2391895
O	0.5706606	-0.4026569	2.0659079
C	1.4018537	1.6241767	1.0943144
C	2.2840284	2.3199730	0.2604727
C	0.6700008	2.3262171	2.0570573
C	2.4435490	3.6984056	0.4014272
H	2.8257739	1.8023943	-0.5246938
C	0.8274818	3.7041678	2.1934343
H	-0.0388896	1.7884824	2.6778006
C	1.7166370	4.3945947	1.3681806
H	3.1286664	4.2289749	-0.2540083
H	0.2446653	4.2405827	2.9370225
H	1.8345293	5.4698332	1.4700207
C	-1.5645146	1.8755461	-0.1683341
C	-0.8095181	2.6664449	-1.0390996
C	-2.6206027	2.4624100	0.5389710
C	-2.9184929	3.8150366	0.3752019
H	-3.1978081	1.8574795	1.2337967
C	-1.1013628	4.0208181	-1.1974084
H	0.0241547	2.2285705	-1.5818840
C	-2.1576735	4.6007432	-0.4936961
H	-3.7388608	4.2577151	0.9341852
H	-0.4939772	4.6253328	-1.8658083
H	-2.3817080	5.6572132	-0.6138861
C	-1.2878012	0.3923442	0.0291443
H	-1.5305778	0.1348998	1.0642232
H	-1.9295704	-0.2074397	-0.6261132
H	1.4990325	-0.6167901	-1.4344388
Cl	1.7439937	1.0112337	-3.3924822

TS-34

56

Energy = -2447.007443789

Ti	0.1469027	0.0777373	2.2694157
N	-1.3067319	-1.2278882	0.1982913
O	0.9344457	-0.1059691	0.5735336
C	0.9242114	-0.9349976	-0.5555136
C	-0.5202262	-1.4211195	-0.7798460
C	-0.8911015	-2.0650113	-2.1011028
C	1.7764952	-2.1937454	-0.2853178
H	2.8227993	-1.9121001	-0.1393980
H	1.7197440	-2.9129925	-1.1076016
H	1.4015224	-2.6732185	0.6221021
C	1.8571658	-1.3953076	3.3091323
C	2.5485847	-0.3760597	2.6318343
C	2.1982491	0.8636897	3.2163703
C	1.3625133	0.5864016	4.3486046
C	1.1458561	-0.7937776	4.3953381
H	0.9535131	1.3124304	5.0357682
H	0.5153804	-1.3123234	5.1004078
H	1.8536474	-2.4472637	3.0598905
H	3.1429427	-0.4957240	1.7396883
H	2.5513722	1.8367203	2.9032682
C	-0.3391591	2.3633094	2.9144621
C	-1.4347374	1.5721102	3.3354877
C	-2.0811538	1.0817998	2.1700187
C	-1.3900759	1.5721060	1.0416646
C	-0.2958419	2.3420067	1.4959693
H	-1.6083042	1.3204358	0.0154257
H	0.4636220	2.8038101	0.8798876
H	0.3491533	2.8955526	3.5536163
H	-1.7081531	1.3472458	4.3571455
H	-2.9216325	0.4048231	2.1533810
H	-2.8586064	-0.1658037	-1.8465895
C	-2.3576514	-0.1116566	-2.8097880
C	-1.3303613	-1.0140858	-3.1121019
C	-0.6970929	-0.9213974	-4.3548764
H	0.1109065	-1.6069415	-4.5941013
C	-1.0709510	0.0597618	-5.2732083
H	-0.5572386	0.1267819	-6.2281993
C	-2.0888191	0.9615098	-4.9605262
H	-2.3750616	1.7319193	-5.6711054
C	-2.7350772	0.8694328	-3.7256990
H	-3.5303148	1.5654965	-3.4727183
C	0.8787950	1.1497616	-1.9709796
C	1.2530630	1.9071562	-3.0760997
H	0.8200128	2.8919709	-3.2277352
C	2.1756460	1.3973120	-3.9943576
H	2.4663755	1.9846769	-4.8608904
C	2.7169656	0.1295387	-3.7919358
H	3.4366495	-0.2758770	-4.4981557
C	2.3339358	-0.6309740	-2.6829514
H	2.7614191	-1.6191979	-2.5482422
C	1.4090748	-0.1300911	-1.7631474
H	-1.7023718	-2.7808045	-1.9239789
H	-0.0392970	-2.6154696	-2.5118186
H	0.1636184	1.5432703	-1.2581496
H	-2.2440052	-1.6218125	0.0699620
Cl	-1.3052398	-1.7168858	3.1257193

35

72

Energy = -5379.702232398

Ti	2.7633928	0.3719894	0.4182232
N	0.6929743	0.0896907	0.1447035
O	2.6441899	-0.8526685	-0.9889488
C	1.4521964	-1.4566586	-1.4687381
C	0.3141160	-0.6533126	-0.8302878
C	-1.1081204	-0.6936266	-1.3252056
C	1.3377655	-2.8997463	-0.9307493
H	2.1768932	-3.4848990	-1.3158898
H	0.4018744	-3.3702211	-1.2407051
H	1.3594776	-2.8871627	0.1596214

```
C     2.1537059   -1.0677899    2.2315835
C     3.3439738   -1.5721247    1.6744778
C     4.3658676   -0.5969893    1.8588271
C     3.8094130    0.4839372    2.5922572
C     2.4351318    0.2224381    2.7806982
H     4.3400266    1.3734167    2.8990881
H     1.7114133    0.8721994    3.2552631
H     1.1808426   -1.5439627    2.2224909
H     3.4565526   -2.5022094    1.1374681
H     5.3917103   -0.6761383    1.5208214
C     4.1855091    2.2445958    0.1588163
C     3.0596510    2.7252043    0.8825604
C     1.9285311    2.6190719    0.0450566
C     2.3535812    2.1156732   -1.2165844
C     3.7425310    1.8916901   -1.1487731
H     1.7042522    1.8902340   -2.0513306
H     4.3631022    1.4645128   -1.9259383
H     5.2031457    2.1885543    0.5209864
H     3.0563511    3.0779603    1.9035180
H     0.9118454    2.8686253    0.3193181
H    -2.0790180    1.5953927   -0.2214397
C    -1.8587647    1.7200701   -1.2783236
C    -1.3991014    0.6288999   -2.0256349
C    -1.1457373    0.7947744   -3.3916215
H    -0.7910434   -0.0446316   -3.9813641
C    -1.3411863    2.0361319   -3.9994758
H    -1.1403675    2.1517749   -5.0610803
C    -1.7877751    3.1242098   -3.2476133
H    -1.9362407    4.0909662   -3.7205943
C    -2.0516369    2.9606695   -1.8856596
H    -2.4135128    3.7976699   -1.2948831
C     2.1903382   -0.4676268   -3.6807542
C     2.1342606   -0.3695299   -5.0703243
H     2.7386804    0.3746143   -5.5813809
C     1.3066053   -1.2229633   -5.8016811
H     1.2581101   -1.1454721   -6.8839518
C     0.5507834   -2.1855404   -5.1313198
H    -0.0874797   -2.8651502   -5.6885927
C     0.6080783   -2.2814770   -3.7399873
H     0.0108474   -3.0391070   -3.2436119
C     1.4176314   -1.4117451   -2.9972884
H    -1.7864268   -0.8236641   -0.4752365
H    -1.2469335   -1.5336607   -2.0080132
H     2.8472397    0.1801664   -3.1149011
H    -0.0369383    0.5884120    0.6776354
Cl   -1.1272894    1.4398284    2.4654132
H    -3.2370720    1.2323785    5.2549309
C    -3.9395506    0.6356056    4.6714905
H    -4.8728792   -0.0561902    6.4998542
H    -4.2379683    1.1811971    3.7710948
C    -5.1407842    0.1212518    5.4530900
O    -3.2160821   -0.5775870    4.2406240
Zn   -2.3676287   -0.4677338    2.3411037
H    -5.9743269    0.8270939    5.4194497
Cl   -1.2318746   -2.3980631    2.0925503
H    -3.6454672   -2.2795408    5.3557435
C    -4.0601615   -1.7635900    4.4842874
C    -5.4510804   -1.2069997    4.7446093
Cl   -4.1839796   -0.2724137    1.0174458
H    -6.0551641   -1.8846554    5.3530073
H    -3.9851232   -2.4032508    3.6032950
H    -5.9658780   -1.0227983    3.7964802
```

BnCN

```
16
Energy = -364.0285071794
C    -2.0430675    0.5051128    0.0000000
C    -0.7898876    1.1153159    0.0000000
C     0.3754730    0.3385407    0.0000000
C     0.2698387   -1.0535583    0.0000000
```

```
C    -0.9868106   -1.6648295    0.0000000
C    -2.1453767   -0.8887713    0.0000000
H    -3.1219549   -1.3642351    0.0000000
H    -2.9399813    1.1180822    0.0000000
H    -0.7155872    2.2001818    0.0000000
H     1.1671534   -1.6665732    0.0000000
H    -1.0554022   -2.7489458    0.0000000
C     1.7187108    1.0592497    0.0000000
C     2.8748581    0.1697049    0.0000000
N     3.7931337   -0.5385174    0.0000000
H     1.7994501    1.7096213    0.8798013
H     1.7994501    1.7096213   -0.8798013
$symmetry cs
```

PhCOMe

```
17
Energy = -385.1325769989
C    -2.3036713    0.5093040    0.0000000
C    -1.0645426    1.1405163    0.0000000
C     0.1192352    0.3843056    0.0000000
C     0.0367940   -1.0171509    0.0000000
C    -1.2057298   -1.6493453    0.0000000
C    -2.3763477   -0.8879518    0.0000000
H    -3.3443096   -1.3812023    0.0000000
H    -3.2148525    1.1005890    0.0000000
H    -0.9891465    2.2235135    0.0000000
H     0.9401746   -1.6186147    0.0000000
H    -1.2612621   -2.7340079    0.0000000
C     1.4306469    1.0982463    0.0000000
C     2.7046192    0.2817120    0.0000000
H     2.7457496   -0.3668557    0.8825647
H     3.5624840    0.9551453    0.0000000
H     2.7457496   -0.3668557   -0.8825647
O     1.4744088    2.3286522    0.0000000
$symmetry cs
```

Et_3N•HCl

```
24
Energy = -753.4829875817
C    -0.6256349   -0.5580367   -1.2903063
C    -0.0349319   -0.4681871    1.1678604
N     0.2722168    0.0242068   -0.2237925
H     0.7412660   -0.0490362    1.8087739
C    -0.0304853   -1.9873176    1.2651483
H    -0.9949752   -0.0378459    1.4639459
C     0.3183125    1.5314914   -0.2983738
H     0.4587085    1.7677063   -1.3556407
C     1.4474375    2.1259331    0.5336078
H    -0.6576901    1.9074181    0.0172376
H    -0.4214539   -1.6295399   -1.3091652
H    -0.2681307   -0.1352273   -2.2317155
C    -2.1057573   -0.2761925   -1.0806909
H     2.4023362    1.6559232    0.2799153
H     1.2707350    2.0238297    1.6073427
H     1.5136173    3.1939182    0.3063271
H     0.9047174   -2.3968388    0.8717881
H    -0.8712650   -2.4403449    0.7328355
H    -0.1129025   -2.2641001    2.3200733
H    -2.4817565   -0.7248478   -0.1567378
H    -2.6581974   -0.7184540   -1.9146930
H    -2.3230702    0.7953009   -1.0662290
H     1.2604665   -0.3295986   -0.4686781
Cl    2.9964373   -1.0101604   -0.9788331
```

Et_3N

```
22
Energy = -292.5922008291
C     2.4362921    0.3800066    0.4101517
C     1.2068969    0.7161185   -0.4327877
H     3.3036275    0.9484250    0.0559424
```

```
H     2.6911092   -0.6836730    0.3556237
H     2.2551415    0.6338948    1.4596200
N     0.0001130    0.0000553    0.0149836
H     1.4091981    0.5128794   -1.5026532
H     1.0065683    1.7885515   -0.3493989
C    -1.2232928    0.6871448   -0.4332484
C    -1.5478512    1.9195757    0.4096853
H    -2.0519100   -0.0227096   -0.3506952
H    -1.1478411    0.9642804   -1.5029800
H    -1.6790971    1.6354465    1.4588060
H    -2.4729970    2.3870446    0.0540483
H    -0.7535950    2.6716573    0.3567979
C     0.0164021   -1.4029034   -0.4332609
C    -0.8882303   -2.2998209    0.4106046
H     1.0453841   -1.7659313   -0.3517383
H    -0.2624585   -1.4762233   -1.5027504
H    -1.9367237   -1.9880221    0.3581710
H    -0.5759935   -2.2708640    1.4595654
H    -0.8307425   -3.3349329    0.0555131
```

$ZnCl_2(THF)_2$

```
29
Energy = -3165.242822512
Zn    0.0000000    0.0000000    1.1271064
Cl    0.4889089    1.9400626    2.0713950
Cl   -0.4889089   -1.9400626    2.0713950
O    -1.4291235    0.4185009   -0.3132555
O     1.4291235   -0.4185009   -0.3132555
C     2.5513189   -1.2749251    0.0820875
C     3.5942831   -0.2875308    0.5838774
H     2.8826381   -1.8179359   -0.8100762
H     2.1677756   -1.9725206    0.8270874
C     3.4266731    0.9247991   -0.3658416
H     4.6032650   -0.7056049    0.5539133
H     3.3658248   -0.0012983    1.6145285
C     2.0255658    0.7491143   -0.9825555
H     4.1871526    0.9187755   -1.1504517
H     3.5027013    1.8666694    0.1807649
H     2.0637616    0.5201984   -2.0510792
H     1.3525977    1.5877927   -0.8036240
C    -2.5513189    1.2749251    0.0820875
C    -3.5942831    0.2875308    0.5838774
H    -2.8826381    1.8179359   -0.8100762
H    -2.1677756    1.9725206    0.8270874
C    -3.4266731   -0.9247991   -0.3658416
H    -4.6032650    0.7056049    0.5539133
H    -3.3658248    0.0012983    1.6145285
C    -2.0255658   -0.7491143   -0.9825555
H    -4.1871526   -0.9187755   -1.1504517
H    -3.5027013   -1.8666694    0.1807649
H    -2.0637616   -0.5201984   -2.0510792
H    -1.3525977   -1.5877927   -0.8036240
$symmetry c2
```

$[ZnCl_3(THF)]^-$

Optimized with Orca using the same method (RI-TPSS-D3BJ-COSMO/def2-TZVP), Grid3 FinalGrid5 TightOpt. The optimization with Turbomole oscillated and did not converge, even if very tight SCF convergence criteria ($scfconv 9) and a large grid (grid 5) were used.

```
FINAL SINGLE POINT ENERGY     -3393.055930334724 (Orca)
Zn   -1.7587537   -0.0761745   -1.7792252
Cl   -2.1818478   -2.2122516   -2.3671818
Cl   -1.2688390    1.4100671   -3.4043734
Cl   -3.0023967    0.7320344   -0.0614486
O     0.1096953   -0.2695502   -0.7894656
C     0.1038876   -1.2232421    0.3335016
C     0.9944786   -0.5916162    1.3967350
H     0.4658297   -2.1761789   -0.0556735
H    -0.9306606   -1.3272146    0.6745036
C     0.7698220    0.9108291    1.1625281
H     2.0444814   -0.8526236    1.2260015
```

```
H     0.7127694   -0.9141291    2.4024399
C     0.7276258    0.9935364   -0.3559021
H     1.5622027    1.5335737    1.5861334
H    -0.1929806    1.2214091    1.5801107
H     1.7284958    1.0347213   -0.7986664
H     0.1161902    1.8068097   -0.7500172
```

$[ZnCl_4]^{2-}$

```
5
Energy = -3620.841967027
Zn    0.0004398   -0.0002198   -0.0000121
Cl   -1.3534796    1.0450728   -1.5581827
Cl   -1.2882736   -1.3877135    1.3302054
Cl    1.6101930   -1.2513564   -1.0937912
Cl    1.0311204    1.5942168    1.3217806
```

TMSCl

```
14
Energy = -869.6784054378
Si   -0.0015526    0.3875877    0.0000000
C     1.7892543   -0.1507268    0.0000000
H     2.3123654    0.2190828    0.8885843
H     2.3123654    0.2190828   -0.8885843
H     1.8482751   -1.2466373    0.0000000
C    -0.8947421   -0.1518459    1.5518507
H    -0.9268971   -1.2478094    1.5999899
H    -1.9248080    0.2205537    1.5655589
H    -0.3826275    0.2145092    2.4482254
C    -0.8947421   -0.1518459   -1.5518507
H    -0.9268971   -1.2478094   -1.5999899
H    -0.3826275    0.2145092   -2.4482254
H    -1.9248080    0.2205537   -1.5655589
Cl   -0.0025582    2.5007953    0.0000000
$symmetry cs
```

THF

```
13
Energy = -232.5924456750
C    -0.0199655    0.7972581    0.7775471
C    -0.0120952   -0.6982686    1.1403056
O    -0.5803319   -1.3713594    0.0000000
C    -0.0120952   -0.6982686   -1.1403056
C    -0.0199655    0.7972581   -0.7775471
H     0.8491932    1.3137456    1.1936000
H    -0.9196382    1.2835264    1.1634380
H    -0.6235216   -0.9526303    2.0089477
H     1.0161934   -1.0579515    1.3011590
H    -0.6235216   -0.9526303   -2.0089477
H     1.0161934   -1.0579515   -1.3011590
H    -0.9196382    1.2835264   -1.1634380
H     0.8491932    1.3137456   -1.1936000
$symmetry cs
```

Appendix E — Coordinates (Orca)

The C-C coupling precursors and the C-C coupling transition states were optimized (again) using Orca in order to calculate the energy barriers for the different radical-radical coupling scenarios.

8

```
38
Coordinates from ORCA-job ti3cl-benzylcyanid
  C   -2.24991950018074     -2.91210767484321      0.87456163204897
  C   -3.49817907321991     -2.25341012285823      0.77131698506279
  C   -3.67389997558447     -1.86965799715314     -0.59076950789850
  C   -2.51771050691624     -2.25468442954606     -1.31510303339382
  H   -4.19616402377884     -2.07904733340182      1.57967308837663
  C   -1.63804577433671     -2.90619220284401     -0.39860992480475
  H   -1.80653790745612     -3.28557681591361      1.78549007172150
  H   -0.65703765663816     -3.29773319804846     -0.62942622180176
  Ti  -1.86355452295773     -0.61101086610429      0.22352000350865
  C   -2.56893832886457      1.35692290943497      1.33080823403932
  C   -1.45083408081319      1.68511702107579      0.51285262453501
  C   -3.62891574128721      0.97173996600950      0.47911495656060
  C   -3.17508197602046      1.07052007336617     -0.86864604494662
  C   -1.83820847028969      1.52299476177693     -0.84643797556889
  H   -4.60784795770872      0.63675160819185      0.79519315849047
  H   -2.58505179778801      1.35413296349530      2.41131183765466
  H   -0.47025272824615      1.97179408579016      0.86560904759925
  H   -3.74652008412466      0.82622897469027     -1.75359486054493
  H   -1.20719906071404      1.67648464224241     -1.71112899881817
  Cl  -0.44955404719178     -0.81457082786132      2.25767704127136
  N    0.02677883730400     -0.62070745471155     -0.73407913336426
  H   -4.53695980378425     -1.36154476655403     -0.99630240546588
  H   -2.33746136079984     -2.09219572934253     -2.36946654528047
  C    1.11452940005304     -0.55659520989077     -1.12713027189567
  C    2.51385260082139     -0.43193239439665     -1.50067372476339
  C    3.27872214740352      0.48120448204572     -0.54440350892364
  H    2.57750319339902     -0.05385620684548     -2.52714118985954
  H    2.94916975673991     -1.44045629635291     -1.50364095571383
  C    4.43039297120096      1.12587572938560     -1.00701958897637
  C    2.86780118658886      0.66104407198775      0.77966391016671
  C    3.61054295853052      1.47715004220630      1.63500106337799
  C    4.76355912853174      2.11533038175504      1.17520086125696
  C    5.17207182406465      1.93784026703163     -0.14850108184354
  H    4.74671964452593      0.99456670630590     -2.03903332423796
  H    6.06513155461605      2.43535348506878     -0.51614887803211
  H    3.28307940488433      1.61434179709904      2.66170585398425
  H    5.33851760510909      2.75162823359628      1.84194850598797
  H    1.96550216492848      0.17425692411270      1.14660850049104
-------------------------   --------------------
FINAL SINGLE POINT ENERGY     -2061.268317775568
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UHF SPIN CONTAMINATION
----------------------
...
Expectation value of <S**2>     :     0.755327
Ideal value S*(S+1) for S=0.5   :     0.750000
Deviation                       :     0.005327
```

9

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39
Coordinates from ORCA-job ti3cl-acetophenone
  C   2.03705374516681     -1.55056161074573     -0.54859985241250
  C   3.20667311788787     -0.76806323412826     -0.69028088373537
  C   3.75136350387399     -0.54650266458986      0.60631993185332
  C   2.92833027958779     -1.21720343089028      1.54136581538824
  H   3.60799102929566     -0.39290456699215     -1.62079881489189
  C   1.86291290212883     -1.82542325134327      0.83638640113802
  H   1.37900657686738     -1.85395909569574     -1.35128503433485
  H   1.03396792031669     -2.35839501249751      1.28075213465218
  Ti  1.61508050170609      0.53620387286533      0.51700766969427
```

```
  C   0.70541404715813      2.35012591316024     -0.78169007092272
  C   1.08405106034596      2.87458955646647      0.47327619977451
  C   1.87032755373290      1.87558057131057     -1.43401696285653
  C   2.98236137223296      2.15351355944400     -0.58863760877364
  C   2.49839732475787      2.74741672055182      0.59716841261681
  H   1.90630532037976      1.39895560475903     -2.40428762324340
  H   -0.30237811353973      2.26998950948027     -1.16439616071741
  H   0.42235976295410      3.27286442908514      1.22717706730861
  H   4.01522464400901      1.91996805068407     -0.80385359063984
  H   3.08844176850687      3.03737237943302      1.45537070140609
  O   -0.26295305641036     -0.10143128646550      0.30876942573325
  Cl  1.19354217479011      0.90734070131730      2.88808367174147
  H   4.63197279286737      0.03702064239989      0.83894968305623
  H   3.05486536575451     -1.21118232079836      2.61343287217064
  C   -1.50769282572498      0.16268895919832      0.41313512701281
  C   -1.96325180768993      1.41315379862577      1.10764759058716
  H   -1.15634294208500      1.77774094068776      1.74426485094112
  H   -2.84877665582704      1.22296472038653      1.72062850389161
  H   -2.23082467043868      2.19278289884486      0.38132494408510
  C   -2.45665062626541     -0.77917571493117     -0.16285831418312
  C   -3.84770333151269     -0.53430557012776     -0.14203060978474
  H   -4.23405110372920      0.37053526666060      0.31568896135314
  C   -4.73502286524153     -1.44212399916502     -0.71112869174059
  H   -5.80163622279596     -1.23717484800208     -0.68830894639349
  C   -4.26071054948030     -2.61358803647569     -1.30959062575685
  H   -4.95646272136259     -3.32110169509336     -1.75113987935216
  C   -2.88360730383003     -2.86885760185206     -1.33772572422174
  H   -2.51016538125919     -3.77773003665683     -1.80148562168564
  C   -1.99216202218351     -1.96471438111766     -0.77693875566776
  H   -0.92525066494452     -2.15640973779269     -0.79769589309034
-------------------------   --------------------
FINAL SINGLE POINT ENERGY     -2082.374154409933
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UHF SPIN CONTAMINATION
----------------------
...
Expectation value of <S**2>     :     0.758545
Ideal value S*(S+1) for S=0.5   :     0.750000
Deviation                       :     0.008545
```

TS-10-anti (broken symmetry)

```
77
Coordinates from ORCA-job TS_006
  Ti  -3.28074695084671     -0.73704770709364     -1.25050295701235
  Ti  3.71842042557891     -0.54379609953658     -0.40573347606659
  N   -1.55048588172371     -0.16882821393135     -0.33891643443716
  O   2.25710262017307      0.75407205920252     -0.55713990962931
  C   1.18522505580922      1.15924527646293     -1.15764759249443
  C   -0.63514946349598      0.10886978341515      0.34188463833890
  C   0.12019573923985      0.16119046081074      1.59875469238374
  Cl  -2.91006931692231      0.68870773602902     -3.20323694384468
  C   0.68042164002233      0.41745892178168     -2.35721745800008
  H   1.22545143315586      0.73525253623718     -3.25692208316301
  H   -0.38249588886792      0.58755228073128     -2.52989907397496
  H   0.84656980554464     -0.65044847483933     -2.20637318168765
  C   -4.07107531652627      0.03509173855585      0.84425702676054
  C   -4.08207319792252      1.14649178894760     -0.05020745330768
  C   -5.00511035412866     -0.91022349243250      0.36892641641482
  C   -5.60163571986330     -0.38816435979970     -0.81895789782709
  C   -5.04583228779997      0.88825351641940     -1.05590984481839
  H   -6.34503883622421     -0.88248535637653     -1.42997046549597
  H   -5.26377054450703      1.52504230952973     -1.89984456756118
  H   -3.44356677048814      2.01701783047391      0.00932376639618
  H   -3.44076022725960     -0.07818795595299      1.71501115072395
  H   -5.22013743751955     -1.86859276683945      0.82004798284052
  C   -4.05924827635544     -2.94145959628796     -1.54463322323589
  C   -2.93281399598068     -3.01589997939784     -0.67817713335329
  C   -1.78797173263535     -2.63897657268551     -1.42578635509824
```

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  C   -2.20637126914738     -2.29074542435069     -2.72887028001768
  C   -3.61569350866996     -2.47385167962956     -2.80732876675619
  H   -1.57522721801059     -1.90346021439045     -3.51483586117087
  H   -4.23647266256037     -2.27307107054263     -3.66968216008658
  H   -5.07925910330085     -3.18326935339673     -1.28245200796664
  H   -2.94477573449046     -3.30881494017407      0.36309389992488
  H   -0.77692163814740     -2.57194525940695     -1.04758205937503
  C   3.51647930986068     -1.25388867794467     -2.67940650951325
  C   4.03668625616709      0.06138931553300     -2.70130008958550
  C   5.30735427641373      0.04108903850034     -2.07842255662007
  C   5.58975825360666     -1.30728889935694     -1.70869364090833
  C   4.48168414335477     -2.10053070708573     -2.06375594975173
  H   6.48446077402699     -1.65687475978920     -1.21340605840025
  H   4.36682913720149     -3.15843347805933     -1.87520065545589
  H   2.55168295011949     -1.56936573973135     -3.04389883185829
  H   3.53847377159018      0.94366665329822     -3.07767761325817
  H   5.95094316618998      0.89580174593041     -1.92038809120343
  C   5.66187067381129     -0.03636097602578      0.87987598612863
  C   5.11924647126689     -1.24102975982098      1.39902241205904
  C   3.87087590724566     -0.92699442141443      2.00018728178288
  C   3.63621614525089      0.45209505996422      1.82888184419137
  C   4.72938588599219      1.00700461830208      1.11275045650828
  H   2.74985973553078      0.98726607764328      2.13294123035987
  H   4.83908958596007      2.03977854115040      0.80952590598530
  H   6.61516949111186      0.06987803712001      0.38391325025561
  H   5.57215227526596     -2.22222207249653      1.34809822479977
  H   3.19885634812106     -1.63518691487257      2.46174790008183
  Cl  2.04691274531893     -2.30093230226607     -0.07425020158192
  H   -1.15377100875196      1.74053758068056      3.42287477313450
  C   -1.38647608627301      0.68739426983088      3.56129401320139
  C   -0.78704316502846     -0.26782710009184      2.73488963807449
  C   -1.09781253950229     -1.62192099851682      2.90887187293699
  H   -0.63686329780847     -2.36509109598664      2.26305505977398
  C   -1.99956015195876     -2.01390636977554      3.89677723020710
  H   -2.23624803509856     -3.06644328023555      4.02489301278690
  C   -2.59953529993006     -1.05587509298748      4.71904842690087
  H   -3.30595900858955     -1.36147260719928      5.48538423247339
  C   -2.28729315914785      0.29456612801828      4.55309715344816
  H   -2.74878334030364      1.04357412186568      5.19033571175810
  C   1.32702035645536      3.23285368930403      0.20420025612639
  C   0.80754683323977      4.44859408881457      0.63471628415685
  H   1.34959534617752      5.03419501426271      1.37269164781855
  C   -0.40287389763410      4.92225116138589      0.11761626325293
  H   -0.80926050992910      5.87099731696030      0.45627125402004
  C   -1.08453364816249      4.16427707649492     -0.84217478068854
  H   -2.02638062277554      4.52382034879035     -1.24822253594762
  C   -0.57429080113405      2.94729448591491     -1.27811535043999
  H   -1.14055856183238      2.35992677195078     -1.99477621391309
  C   0.64212397563112      2.45221173647656     -0.75524723267719
  H   0.49234124364851      1.18141345078778      1.73916058353770
  H   0.98102592243457     -0.50535566884332      1.47701332800157
  H   2.27291576673724      2.87015087198734      0.59232869063823
-------------------------   --------------------
FINAL SINGLE POINT ENERGY     -4143.659734482052
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UHF SPIN CONTAMINATION
----------------------
...
Expectation value of <S**2>     :     0.661749
Ideal value S*(S+1) for S=0.0   :     0.000000
Deviation                       :     0.661749
```

TS-10-syn (broken-symmetry)

```
77
Coordinates from ORCA-job TS_opttzvp
  Ti  -1.91936829825979      1.73763570476589      1.49301615796810
  Ti  3.31469910723855     -0.75249777371244     -0.77276252060713
  N   -1.19723562466125      0.24876517599908      0.29664915007056
  O   1.57495060430023     -0.19748518159744     -1.36179987022753
```

C	0.60797618061541	-0.35420743383381	-2.23291300626793
C	-0.95651570942615	-0.74232330619639	-0.30031483724340
C	-1.07139196514735	-2.21746651374272	-0.41346944277206
Cl	-0.17746427477259	3.38995780769641	1.03447798415931
C	0.56315345685948	-1.62473463204030	-3.04100673282551
H	1.03638206967416	-1.47239472776305	-4.02183830616554
H	-0.46340513391443	-1.94964666577143	-3.23125210112232
H	1.10187528858833	-2.41574451246464	-2.51699086166148
C	-2.57301836409901	0.45601989861131	3.39079671602312
C	-1.25581359181364	0.05279197054040	3.07033087805766
C	-2.52356175223930	1.81936236979408	3.80628198442628
C	-1.18842247788452	2.25997542990001	3.70379967720291
C	-0.40060781337683	1.16848089413090	3.23613413324490
H	-0.83049187646438	3.25992100255205	3.90072144556124
H	0.65712765428266	1.20119297273093	3.02140292552460
H	-0.97229983161916	-0.92850654896315	2.71982233647905
H	-3.45427466590389	-0.16706961989975	3.33516056852216
H	-3.36688370991421	2.41989817603553	4.11805166748052
C	-3.71854770057503	3.25884997947203	1.26316235919170
C	-4.27121593921238	1.95843270777182	1.44300731708054
C	-3.89976965260924	1.16533856877982	0.33224141798479
C	-3.14587306288788	1.98752721607421	-0.55676632483933
C	-3.04826424773641	3.27346640459979	0.01407714542437
H	-2.68656139060312	1.67346246605763	-1.48226709220450
H	-2.49322210975959	4.10262227762208	-0.39605205906649
H	-3.79820283385238	4.08807507940415	1.95358140305159
H	-4.85784185386183	1.63020051071559	2.28851052800275
H	-4.14106119575433	0.12209380844406	0.18463628070685
C	4.01451973476820	-1.69358133551359	-2.86114183576396
C	3.73026778919343	-0.33547470455325	-3.10800520927251
C	4.63115315354521	0.45250437625401	-2.34698664790461
C	5.51877099797198	-0.43394689387497	-1.67387845818453
C	5.12357972492365	-1.75658826839383	-1.96381464182688
H	6.33430849324472	-0.13948934256037	-1.03000301325958
H	5.56732662480137	-2.65879668447138	-1.56634316577487
H	3.47067844184874	-2.54220323698274	-3.24827517561341
H	2.92522443521798	0.05031382904954	-3.71709572030502
H	4.65402113389100	1.53295384632163	-2.30846131279742
C	4.10688912879875	0.99091251279311	0.66502104730648
C	4.67647505904395	-0.22963456476628	1.13849889421334
C	3.62342027416163	-1.05041791171888	1.59296856855671
C	2.40331181480690	-0.34837856804361	1.39955797493286
C	2.70801370939873	0.92288447903183	0.85486755204328
H	1.41377771727796	-0.73487670982037	1.59301220460684
H	1.98273605838482	1.67564573628604	0.57736490884639
H	4.65278038800991	1.82565662269234	0.24752948846256
H	5.72587080833608	-0.48728085507846	1.14512372587742
H	3.72321238646677	-2.05588973485516	1.97369662467062
Cl	2.63652550268056	-3.07001400303220	-0.44983712220897
H	-3.61085845472494	-2.26601754419948	0.62707198877573
C	-2.88159542680004	-2.71718252515719	1.29498446260810
C	-1.54216815672786	-2.80779107298371	0.90050031690496
C	-0.60892737675500	-3.39070530035629	1.76569128941996
H	0.43212156240083	-3.45771247382977	1.45815258009389
C	-1.01085292777182	-3.87424784780965	3.01215964706202
H	-0.27933752481624	-4.32446702070590	3.67734778991308
C	-2.34702809938295	-3.77461357838561	3.40403952094990
H	-2.65968469465247	-4.14532284890414	4.37600671777321
C	-3.28264503703934	-3.19954155122731	2.53982393525586
H	-4.32488492950998	-3.12523254183800	2.83776835513608
C	0.11800855832503	2.07698629088231	-2.08736046482562
C	-0.54687669585707	3.21197071531888	-2.53451544179843
H	-0.34915882808389	4.16508657965719	-2.05322629962106
C	-1.47731655441312	3.12693668242663	-3.57449464234748
H	-2.00096852294391	4.01444499591670	-3.91804698044193
C	-1.73591726662927	1.88266566519835	-4.16301388621221
H	-2.46067485526825	1.80285808141229	-4.96902072646795
C	-1.06849180746795	0.74386865494618	-3.72629119465126
H	-1.27910086366720	-0.20854204946016	-4.20205351881650
C	-0.12069952568529	0.81933573155617	-2.67828461885154
H	-0.09067403883908	-2.62160834297607	-0.67774053873455

```
  H   -1.76155062593801     -2.44457057864100     -1.23326091757151
  H   0.82156943026530      2.14710778468355     -1.26846498131733
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FINAL SINGLE POINT ENERGY     -4143.652709527300
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UHF SPIN CONTAMINATION
----------------------
...
Expectation value of <S**2>     :     0.499862
Ideal value S*(S+1) for S=0.0   :     0.000000
Deviation                       :     0.499862
```

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53
Coordinates from ORCA-job ti3-dinitrilekat
  C   -1.94749575645987     -2.63489564720914      0.11771804723419
  C   -3.21920436266661     -2.46238590604672      0.74121875061647
  C   -4.18639837532801     -2.34532512186610     -0.28562417523649
  C   -3.51808073990147     -2.43729990757326     -1.54149963767860
  H   -3.40754664128010     -2.41904820460183      1.80547284475946
  C   -2.14212857678310     -2.63504204220969     -1.28779442193984
  H   -1.00157182211827     -2.74533021424580      0.62943886165887
  H   -1.36789444000287     -2.72617607456118     -2.03690531749908
  Ti  -2.74349402661361     -0.48645584759619     -0.42264822849069
  C   -2.94093158185090      1.83016307506122     -0.74452539116277
  C   -3.47992632732134      1.18298353862593     -1.89615379533512
  C   -3.77172012586699      1.51827886890142      0.36429395407069
  C   -4.80104579017619      0.66182952569925     -0.08540573298018
  C   -4.62700782825594      0.46354347658347     -1.48655290932581
  H   -3.61981558129385      1.84283038688634      1.38444170316080
  H   -2.05202816500121      2.44519306868951     -0.72021786637516
  H   -3.07458737882575      1.22178948830545     -2.89815221075785
  H   -5.58359523850921      0.23450891013811      0.52665341875101
  H   -5.25749243096996     -0.14234232920854     -2.12233335110931
  N   -0.87331636695584     -0.09838954890001     -1.35315212273747
  H   -5.24825618923328     -2.20063080745822     -0.14442399987699
  H   -3.98095842843510     -2.37194789425102     -2.51679071183242
  C   0.20809068335401      0.11834065782011     -1.70711114853731
  C   1.58453618214159      0.36107296998258     -2.09925193068722
  C   2.59144580985398     -0.43213993103516     -1.27052015226713
  H   1.77162626773657      1.43736892164406     -1.99562460496570
  H   1.68399411599653      0.11990606737796     -3.16526662278928
  C   2.20089863649378     -1.34795959294601     -0.29376605279334
  C   3.95309670411149     -0.21791246150750     -1.50859586187856
  C   4.91062018425908     -0.91482491474880     -0.77466216075609
  C   4.51691606345313     -1.83059333997654      0.20398534429259
  C   3.16052489404161     -2.04608534910675      0.44176121976918
  H   1.14565424208262     -1.51619157572571     -0.09797819845977
  H   2.84498744712813     -2.75480621810411      1.20193545301737
  H   5.96552292067139     -0.73840658548494     -0.96371660382088
  H   5.26452521042074     -2.37083592214335      0.77725189295667
  H   4.26415042374292      0.49936634570631     -2.26361704122051
  H   -0.16776781251217      1.49070298382928      3.66112118826971
  H   0.06767579948499      2.79002893495862      1.09435168651707
  N   -1.56517279105842     -0.02372440785328      1.28047205558089
  C   -0.77994895896820      0.30781954269454      2.06539269849837
  C   0.27503521440529      0.78369370672587      2.94812519793213
  C   1.09493274791892      2.45857457266484      1.22501727582186
  H   0.65683502341869     -0.06492474172682      3.52474916055997
  C   1.38898625329945      1.43692248781950      2.13374653587976
  H   1.88275087536813      3.85332766154666     -0.21108260094540
  C   2.11711913534515      3.05702286805099      0.48962534644804
  C   2.70948318561364      1.01391204011530      2.29642210614448
  C   3.43803245180225      2.63500510970977      0.65734664408251
  H   2.93902518082693      0.21072050800986      2.99095139357557
  C   3.73190386274061      1.61555150439640      1.56237604883037
  H   4.23410502553269      3.09710823614643      0.08113043898040
  H   4.75491129514399      1.27610882799689      1.68837368405058
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FINAL SINGLE POINT ENERGY     -1964.888427963400
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UHF SPIN CONTAMINATION
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...
Expectation value of <S**2>     :     0.755645
Ideal value S*(S+1) for S=0.5   :     0.750000
Deviation                       :     0.005645
```

TS-26 (broken-symmetry)

```
92
Coordinates from ORCA-job TS_opt
  Ti  -3.30875599790615     -0.65737075409702      1.02359381724449
  Ti   3.17215775543741     -1.93604629653825      0.85896209339996
  N   -1.50542248271342     -0.31998327235266      0.21975274129133
  O    1.89239348370950     -1.75084241369105     -0.58296500521917
  C    0.72662078690980     -1.92032911208206     -1.13609321120283
  C   -0.43116664068454     -0.01278064341035     -0.16799629291840
  C    0.52746220593062      1.06858939166994     -0.43576712013326
  N   -3.20619206351403      1.43938762092977      1.38180038799181
  C   -0.21962818452426     -2.95967626064047     -0.61555228981070
  H    0.05617293901938     -3.23713186775259      0.39869092671780
  H   -0.20001901856992     -3.85413250416057     -1.25123680629874
  H   -1.24792330047867     -2.58436366178144     -0.59514552616350
  C   -1.90683012236844     -1.88480656607102      2.49751399129180
  C   -2.20781837251694     -0.64124438039279      3.10478054011265
  C   -3.11450261908151     -2.60644847742520      2.34844059150882
  C   -4.16637186957772     -1.81739172948969      2.90190605179035
  C   -3.61032994552465     -0.60362657300754      3.36318540699174
  H   -5.21150075614446     -2.09081392047841      2.94237069313384
  H   -4.15552022379207      0.21537653189207      3.81222978625344
  H   -1.49186258848198      0.13987108411574      3.31544285408629
  H   -0.92448865534063     -2.18255560731152      2.16359487556498
  H   -3.22224630900841     -3.58382439915223      1.89735799916177
  C   -5.04601714773458     -1.90056645447668      0.05841586485377
  C   -3.99346377355744     -1.84099466901360     -0.89174419287327
  C   -3.85696997644800     -0.48442764982483     -1.30158171116640
  C   -4.81382296003793      0.28394559338296     -0.60131506688369
  C   -5.53874902118307     -0.58083590641062      0.25929038032731
  H   -4.94364426525998      1.35451949413055     -0.67477424292955
  H   -6.32989676365860     -0.28961716326708      0.93706185888364
  H   -5.40688722516246     -2.79474903727492      0.54574814619989
  H   -3.42307128787325     -2.68369943785478     -1.25732882574577
  H   -3.13087222700980     -0.10668664297814     -2.00700528520731
  C    2.05883936038933     -3.80886035844762      1.87205747606961
  C    2.56085091722659     -4.25150916863128      0.62940626672592
  C    3.97427883869853     -4.16422876354091      0.66973190092943
  C    4.34446447771205     -3.71422996819788      1.97048553183246
  C    3.16574629692162     -3.47072988617731      2.70200145150668
  H    5.35274454414781     -3.55821834564300      2.32546402354320
  H    3.10646137666546     -3.07641249688577      3.70647233156391
  H    1.02174755750166     -3.71850831802398      2.15780501222406
  H    1.97858996689977     -4.55399958128673     -0.22861087262724
  H    4.64877611323231     -4.41807530397280     -0.13640191135087
  C    4.77106887394838     -1.07123922680345     -0.71230813587130
  C    5.49309330096720     -1.61362240575308      0.37800426513672
  C    5.19329940851058     -0.84406259520371      1.53475636507070
  C    4.31619804554182      0.19932903080300      1.14356359128451
  C    4.06082911461358      0.06191931154160     -0.23656525108696
  H    3.88233064696416      0.93900077069486      1.79884803342256
  H    3.41845652060320      0.69637649012898     -0.82749674829516
  H    4.76504620422179     -1.45480207355812     -1.72383986022941
  H    6.15087929542006     -2.46911327281884      0.33523551390351
  H    5.56594470239346     -1.01866226643027      2.53493100327588
  Cl   1.65725660562387     -0.74806483028578      2.28613230833994
  H    2.04384051113312      2.52752528296399     -2.11576277119917
  C    0.98695182714525      2.74492077115868     -2.24520161055759
  C    0.04006184850625      2.05266483801697     -1.48503758523333
  C   -1.31494145932637      2.33172332390898     -1.67171962718188
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  H   -2.05630546963280      1.79187821234623     -1.09218561176506
  C   -1.71970680422650      3.29877197747079     -2.59212969948711
  H   -2.77812357141865      3.50419919324044     -2.72837900819882
  C   -0.76929314194101      3.99800414214391     -3.33697245868340
  H   -1.08204034209316      4.75123027220577     -4.05435968296026
  C   0.58712151399544      3.71606423114448     -3.16092681433503
  H   1.33483041345682      4.24871498111766     -3.74197136162683
  C   1.58146586789010     -0.63773750055607     -3.09216627348646
  C   1.38724979157559     -0.02224319981054     -4.32373096270401
  H   2.20461833151731      0.52234595607834     -4.78761366696596
  C   0.14629207598196     -0.09498988545970     -4.96015445267455
  H   -0.00819339006300      0.39664665202338     -5.91585381047162
  C   -0.89554442504234     -0.81280731108895     -4.36219803935252
  H   -1.85996118561024     -0.88379662542820     -4.85724159495305
  C   -0.70572982521197     -1.43405289389440     -3.13420404151900
  H   -1.52402060945894     -1.98223880566296     -2.68007971088453
  C   0.53235988285189     -1.33940894069934     -2.46451198147490
  H   1.48287283934434      0.63545389089019     -0.73411201621474
  H   0.69185701288548      1.57862843746713      0.52324673242029
  H   2.54550460782660     -0.58850586795180     -2.59898866775975
  C   -2.89684186897909      2.54472857948757      1.53796783886741
  C   -2.36070668724654      3.88664916781541      1.72226719938243
  C   -0.83572559340504      3.83191751367529      1.77969895489573
  H   -2.78332036778500      4.30669550119458      2.64294202572420
  H   -2.69890108600033      4.51034741616475      0.88856560004173
  C   -0.19505292839576      3.09941226354033      2.78566145154758
  C   -0.07547111167262      4.50006667139783      0.81855753509003
  C   1.31859684719078      4.44385132098288      0.86822929577589
  C   1.95574404654807      3.71127587612864      1.86983585483505
  C   1.19641629105046      3.03701314577494      2.82971723156905
  H   -0.78330541696921      2.57564488878971      3.53480965085795
  H   1.68500758523101      2.45476287476599      3.60437604926249
  H   3.04023540278805      3.66204461125582      1.90070669019120
  H   1.90312175277208      4.96219631097800      0.11444293825829
  H   -0.56869770626895      5.05136866972990      0.02317067534896
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FINAL SINGLE POINT ENERGY     -4047.276426446711
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UHF SPIN CONTAMINATION
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...
Expectation value of <S**2>     :     0.377894
Ideal value S*(S+1) for S=0.0   :     0.000000
Deviation                       :     0.377894
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24

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54
Coordinates from ORCA-job opt
  C   1.84884952334400     -3.10277250939331     -0.47216148359588
  C   3.21467588087006     -2.95656925077860     -0.81613465280066
  C   3.88125047259928     -2.31883748670128      0.26921903598154
  C   2.92778652300180     -2.08110575519506      1.28358916006554
  H   3.67055622260317     -3.27080389408361     -1.74472228215304
  C   1.66767634322135     -2.55012428233084      0.82506252215749
  H   1.08041116210928     -3.52959186337568     -1.10217579651854
  H   0.73159944664151     -2.47318301480892      1.36074799079606
  Ti  2.27797091541911     -0.78706602822502     -0.62565154585869
  C   2.09841383011298      0.51961100752033     -2.63176644708533
  C   2.70220610318316      1.32423832328519     -1.63822219662693
  C   2.95160697570039     -0.58080111210557     -2.88968296171152
  C   4.11019257721330     -0.43056421345297     -2.07457857711027
  C   3.94995817118046      0.73101421341134     -1.28283700330727
  H   2.76274187012680     -1.38250801844886     -3.59114309648360
  H   1.13239299805539      0.68413229505593     -3.08803947551844
  H   2.29596754568489      2.23089501540912     -1.21252033078678
  H   4.95711114547824     -1.10102558959020     -2.05162071198452
  H   4.64987097667774      1.10879128168052     -0.54969802692837
  O   0.24310594295100     -0.72888869253876     -0.79657969712998
  N   1.89182071216029      0.52812299838014      0.99260251609069
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  H   4.92848460177163     -2.05173199422725      0.30716944076194
  H   3.11887534730533     -1.59234988123908      2.22876721469083
  C   -0.83460908096496     -0.08071989947592     -0.90690624914719
  C   -0.82795283723373      1.40820316747121     -1.09141667867015
  H   0.16999644370381      1.80201579434740     -0.90983871673136
  H   -1.53678873090868      1.88330603441685     -0.40685994853021
  H   -1.13428362702100      1.66866919749032     -2.11229703552936
  C   -2.09930831604750     -0.81180385322960     -0.83797450625352
  C   -3.32990833108449     -0.15723406291140     -1.04010666558013
  H   -3.35353496059011      0.90271418191908     -1.26912729144511
  C   -4.52480914970976     -0.86240255500765     -0.94516737861097
  H   -5.46842507061992     -0.34933145029373     -1.10385473936401
  C   -4.51171627281349     -2.22627706392459     -0.64099858004625
  H   -5.44634706716897     -2.77343250571892     -0.56058453029494
  C   -3.29432286231869     -2.88809668894564     -0.44135428333546
  H   -3.28432449208140     -3.94809573962710     -0.20596106873026
  C   -2.09871586449061     -2.19000688469285     -0.54401857091722
  H   -1.15132760575915     -2.69419969109390     -0.39097212509127
  C   1.46787138169054      1.18837877861611      1.84422330000561
  C   0.79715161149809      1.98674026593454      2.86041071589645
  C   -0.69691477597446      2.03184410513198      2.55035727222546
  H   1.23226832899787      2.99081319993958      2.86587220727308
  H   0.99471290848477      1.53136143932959      3.83836595240097
  C   -1.45258088044816      0.85429670915666      2.57232649007748
  C   -2.80922710907277      0.88792744752341      2.25723419867183
  H   -0.97948320104567     -0.09002496220554      2.83012346120447
  C   -3.41828249653760      2.09859195787641      1.91752339030485
  C   -2.66646454557635      3.27409741458675      1.89727051852164
  C   -1.30492481768600      3.24114561748692      2.20907504337320
  H   -0.71777184059496      4.15518196800842      2.18389653104627
  H   -3.13529956534394      4.21761268336756      1.63408958339485
  H   -3.38857841146096     -0.02995006024495      2.26916893042083
  H   -4.47456404923290      2.12406390652141      1.66712717851614
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FINAL SINGLE POINT ENERGY     -1985.990499647922
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UHF SPIN CONTAMINATION
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...
Expectation value of <S**2>     :     0.756840
Ideal value S*(S+1) for S=0.5   :     0.750000
Deviation                       :     0.006840
```

TS-27 (broken-symmetry)

```
92
Coordinates from ORCA-job TS_opt
  Ti  -3.71735279542717     -1.28764420062573     -0.23398468190174
  Ti  3.39129143281474     -0.36050425700842     -1.53517640261241
  N   -1.85604967852836     -0.49449101249062     -0.12488485692664
  O   1.57448075572870      0.27724329495137     -1.72238059455879
  C   0.32638722103126      0.29987508578955     -2.08294119362310
  C   -0.79685441112563     -0.00433696195373      0.06712327323087
  C   0.23024819337936      0.50112682439448      0.98823156928632
  Cl  -3.98758654045534     -1.04609872385276     -2.62081041552345
  C   -0.27885708675196     -0.93990108107663     -2.67584093690162
  H   -0.03608540989889     -1.00422852550462     -3.74523935451137
  H   -1.36544675338445     -0.94581439644669     -2.58067803155901
  H   0.12082895694674     -1.82459952226499     -2.17595409806454
  C   -3.99565757294032      0.47900655236109      1.32429618172963
  C   -4.33828648974096      0.98752306498044      0.03708930696389
  C   -4.92738401016019     -0.52764796488443      1.65511359516701
  C   -5.85670907303947     -0.64136115603964      0.57659313585517
  C   -5.50141612017523      0.31077689064558     -0.40378029732416
  H   -6.69125197090092     -1.32684412117459      0.52273255547237
  H   -5.99419376206759      0.45347452686134     -1.35331145815634
  H   -3.79910321720006      1.74257167771861     -0.51730323178409
  H   -3.15824720820895      0.79339669186105      1.93113381083017
  H   -4.93497906447919     -1.11341939333380      2.56334755368247
  C   -4.49704377008661     -3.32090915812856      0.69636478796818
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C	-3.21934683588066	-3.05655048978321	1.26205116011338
C	-2.26065949650619	-3.15279154580402	0.22151362284386
C	-2.94004761279115	-3.42759367273596	-0.98486050829116
C	-4.32878543984741	-3.53068271427958	-0.69294015423719
H	-2.49144265540703	-3.50233898698151	-1.96423459293324
H	-5.11630874919084	-3.70993283291287	-1.41136922512175
H	-5.43432053627270	-3.34269339002412	1.23306741679352
H	-3.01955954688760	-2.83617366838122	2.30057910246263
H	-1.19794607208610	-2.99094257601952	0.32012243544256
C	2.88343185362305	-2.23228655329495	-2.89102889666775
C	2.99222827191200	-1.11286311491541	-3.75266152537851
C	4.32612385666719	-0.64487544506855	-3.69530758086491
C	5.05740232743047	-1.50635593060797	-2.82429351200542
C	4.16964959732506	-2.47715445022694	-2.32451475019756
H	6.10433519461375	-1.41628881648601	-2.57175418668512
H	4.41554974713769	-3.26004055619898	-1.62050835844672
H	1.98999007847608	-2.80596233986886	-2.69462871685242
H	2.19352950575808	-0.66018651359773	-4.32223138058190
H	4.72232141005198	0.20816078571289	-4.22924610429693
C	4.17497232922761	1.89411041061834	-1.45387073682465
C	5.30584389687186	1.02967854558593	-1.42300843193995
C	5.26141984134503	0.28405283132418	-0.21961330536873
C	4.12395026836716	0.72452982188701	0.51493030128605
C	3.46744196311048	1.71895203176377	-0.23865978060421
H	3.81299713682513	0.35104794104722	1.48046276321105
H	2.55032229102686	2.21818549784307	0.03912771236426
H	3.92220711816834	2.57903358924393	-2.25230416067242
H	6.06511491923546	0.95991016779634	-2.18761848024481
H	5.96637530038980	-0.47472242138083	0.09216107762917
N	2.78482296421927	-1.67869573523960	0.01172670405707
H	1.70511111585186	1.89172044226523	2.75052382812498
C	0.90021771248269	2.49892767232260	2.34542849395418
C	0.01541077218542	1.94711828623152	1.41047832166172
C	-1.01275181084897	2.73761701195164	0.89797725237805
H	-1.68301032613566	2.33064356813889	0.14771021938124
C	-1.16437435690930	4.06009025070779	1.31673909417753
H	-1.96525972983921	4.66469353142075	0.90146622277211
C	-0.28495980392800	4.60496837370400	2.25131234679525
H	-0.40087018297965	5.63475209452843	2.57643184502493
C	0.75193732758751	3.81998856155010	2.76306479879132
H	1.44523870659407	4.23606874057635	3.48852527885780
C	0.47881449938165	2.78405546935663	-2.12242804138743
C	-0.09557250053648	4.04042895523714	-2.26967519656087
H	0.51753143129597	4.92949920346425	-2.15174194445813
C	-1.45644271575767	4.16289751887345	-2.56470781109028
H	-1.90755645233162	5.14491538790156	-2.67175417965561
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H	-3.28778203199668	3.09436222784599	-2.96478493166890
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H	-2.28905591920659	0.86800300783808	-2.69044746647709
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H	1.21271560824747	0.39499729632839	0.51627727053388
H	0.21880285014441	-0.15007775294921	1.87243769200094
H	1.53500896237921	2.68741534755474	-1.90455250826946
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C	2.10807672843815	-3.18619105218789	2.03729528515561
C	1.34225652077767	-2.31338674600403	3.02573630663008
H	3.02363753318347	-3.59479851739076	2.48182277750600
H	1.50023486580318	-4.03021540795409	1.69591840999027
C	-0.02582892956871	-2.51229201306148	3.22130424739956
C	1.99717588198523	-1.27814363362605	3.70180855439922
C	1.28225764120846	-0.43737430440431	4.55325912323547
C	-0.09083123220484	-0.62346588696387	4.73139378526972
C	-0.74092896610831	-1.66727208034383	4.07270593370808
H	-1.80443561853454	-1.82525127760711	4.22494024463177
H	-0.52927001502408	-3.32982585524661	2.71346325545730
H	-0.64906561441981	0.03853800154650	5.38603834652785
H	1.79514580855783	0.36474752600229	5.07484230232941
H	3.06461371615910	-1.12763867818117	3.56192752920503

FINAL SINGLE POINT ENERGY	-4047.272325562742

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UHF SPIN CONTAMINATION
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Expectation value of <S**2>     :     0.379137
Ideal value S*(S+1) for S=0.0   :     0.000000
Deviation                       :     0.379137
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23

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Coordinates from ORCA-job opt_tzvp
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  N   -3.03509135615391      1.05609036701355     -0.04863876556848
  O    2.05139764409661     -1.13668940751488     -0.49941202930956
  C    2.02520097151059     -2.40980174490150     -0.47979331469777
  C   -3.14073866596895      2.20727269554765      0.02925184057066
  Cl  -0.48070133554927     -0.14177074338253      1.08993383180694
  C   -2.10763213173395     -0.53436950888635     -2.22586601002492
  C   -1.11301573696146     -1.42633062947599     -1.76401009689162
  C   -3.36393906943544     -1.20628146898288     -2.18256547761010
  C   -3.12626155915755     -2.51999955818788     -1.70333402937726
  C   -1.73573564002432     -2.64961029923592     -1.42023871425402
  H   -3.87233259997548     -3.28992907449260     -1.56897120220445
  H   -1.24427476720667     -3.52957592183869     -1.02798890081086
  H   -1.94963808617049      0.48664181930552     -2.54302663441177
  H   -4.32000570389074     -0.79393714444602     -2.47595393333626
  C   -3.51128946153016     -2.87896888371215      1.24732334585389
  C   -4.62460433122800     -2.07834971403072      0.85637831692535
  C   -4.51181324537448     -0.82836883642373      1.50195952852511
  C   -3.31753186091782     -0.83885646425649      2.27445427689903
  C   -2.70718467964892     -2.11777808777304      2.12491727574332
  H   -2.93242291520376     -0.01782808193065      2.86254550039711
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  H   -3.30874224418971     -3.88803671866923      0.91500605235036
  H   -5.41221439743575     -2.37163617621025      0.17601692888823
  H   -5.19316358937852      0.00434229767252      1.39376393294970
  C    2.28195065425231     -0.34331559296086      2.54734437092713
  C    3.50569879125482     -0.32315411240475      1.83585346097779
  C    3.85150123107117      1.02766894515378      1.59700732924877
  C    2.85208050297404      1.84818553272367      2.19952505920388
  C    1.87944657678924      1.00467648366545      2.77312547287992
  H    2.82859059716731      2.92877331847499      2.19394117364002
  H    0.97540046590464      1.31848103077544      3.27401159497074
  H    1.73682262321463     -1.22009242960410      2.86122808807251
  H    4.06021014672728     -1.18436427761806      1.48850746798422
  H    4.72338813411592      1.37399377188529      1.05909804857519
  C    2.58215415119360      2.61528181855832     -0.59619362003837
  C    1.21307237137521      2.80831854992365     -0.27060496744231
  C    0.45206264615322      1.92342615979964     -1.07473449791227
  C    1.34313184477459      1.17370021861880     -1.87331053501148
  C    2.66824186145022      1.58438317406702     -1.56750894550977
  H    1.07014461190610      0.39491936904468     -2.57010734470717
  H    3.57788579772568      1.19178482792581     -2.00172246462492
  H    3.41694547921941      3.15480895234213     -0.17339090843274
  H    0.81962152062845      3.50177545461218      0.45878455532247
  H   -0.61977388619939      1.80551959688670     -1.04093815224058
  C    1.59116544558792     -3.12793056278539      0.76304139452773
  C    2.41507944543432     -3.11668541897081     -1.69248233906013
  H    0.86083614991266     -2.50951936347277      1.28808867174205
  H    2.45119121206889     -3.29290299017438      1.42574251828673
  H    1.15378212471267     -4.10284633594985      0.54322500566785
  H   -0.06818211595528     -1.19477981476439     -1.63342999560666
  C   -3.18709999563922      3.65252332093662      0.18446001517717
  C    2.40742829945837     -4.52582918859532     -1.77087205925235
  C    2.81520349224210     -2.37834968181889     -2.82903290572868
  C    2.77699682163149     -5.16860288860444     -2.94760856983848
  C    3.17830142678138     -3.02565205883075     -4.00116491238464
  H    2.83695597612554     -1.29624419500290     -2.76836743888320
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  H   2.11548543471513     -5.12084543854477     -0.91236166544604
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  H   2.76597862567346     -6.25345847217616     -2.99389731481330
  H   3.48063872938067     -2.44521887738387     -4.86790240848477
  H   3.44444417194869     -4.92983326736716     -4.98509741631675
  C   -2.00750092017534      4.17115723285882      1.00281434914337
  H   -4.14001014927889      3.91096349908560      0.66549879529285
  H   -3.19775837401265      4.10588726052271     -0.81228498349137
  C   -1.37625159779931      5.35674033694820      0.61776081109172
  C   -1.57088557750081      3.49442554654530      2.14561638433979
  C   -0.52069312682110      4.00865080934076      2.90503305950622
  C   0.10555674653864      5.19703536778711      2.52373546610303
  C   -0.32332110692405      5.86917079752103      1.37780988016181
  H   0.16418196384341      6.78938160593879      1.06978121572698
  H   -1.70496210295645      5.87897557987109     -0.27679710163115
  H   -2.04264264969023      2.56096000901773      2.43934233430247
  H   -0.19153291337040      3.48169101727357      3.79549012638024
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FINAL SINGLE POINT ENERGY     -3683.230908243641
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UHF SPIN CONTAMINATION
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Expectation value of <S**2>     :     2.013707
Ideal value S*(S+1) for S=1.0   :     2.000000
Deviation                       :     0.013707
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TS-28 (broken-symmetry)

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Coordinates from ORCA-job TS_tzvp
  Ti  -2.75037778449340      0.17420748318319      0.51807393888795
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  N   -1.22454089046441     -0.73535060804919     -0.43526744109332
  O   1.31049988637706     -0.21824864829238      1.05429585010638
  C   1.78502410031168     -0.57635080645537     -0.09550900460028
  C   -0.41227703360725     -1.34748639146806     -1.03566600543583
  Cl  -1.41586482918241      1.00173023421967      2.50123494725237
  C   -2.26502694707579      2.45588920808242     -0.07413552944085
  C   -2.18910444806842      1.70264354553234     -1.26332070785917
  C   -3.59553658085804      2.37588204021748      0.42063134868071
  C   -4.34370119081706      1.58705823323109     -0.49113117358323
  C   -3.46769974455644      1.13764366930102     -1.51548486308862
  H   -5.39629665800546      1.35871381477245     -0.41237438463828
  H   -1.44905640168617      2.97704542114575      0.40310513168164
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  C   -3.54058042587588     -2.05219238934659      0.32913123901679
  C   -4.66731809465500     -1.20460299425099      0.27775224653233
  C   -4.78441226342306     -0.54654219619986      1.53927000270952
  C   -3.73125402707084     -0.99396599896824      2.36208370675525
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  H   -3.53994048249587     -0.66028778459444      3.37146780264507
  H   -3.18504508225037     -2.68231784337176     -0.47339790475514
  H   -5.32534746298842     -1.07805186907551     -0.57041771352491
  C   -0.29375324221731     -1.42582660206524      4.00065611436630
  C   0.51528093186618     -2.06703322063318      3.03709170375298
  C   1.87466465278237     -1.84356332748164      3.38639958560922
  C   1.89546321906217     -1.07317596618329      4.57420453791473
  C   0.55351115333188     -0.79151708313331      4.94324942837129
  H   2.78214611899986     -0.75220713285016      5.10115572220079
  H   0.23103114697532     -0.20373014917530      5.79166306800251
  H   -1.37155890692397     -1.38644887295557      4.00656772367543
  H   0.16820840016792     -2.59095454820436      2.15807413884764
  C   2.96599529287209      1.46274699683916      3.36423329088021
  C   2.02980167709601      1.80340923054618      4.38611788422867
  C   0.96148126838091      2.49548448307870      3.78789363027046
  C   1.25427839780454      2.62977523813748      2.39566707943300
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  H   2.97749010256053      1.92198552638866      1.18315748273042
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  H   2.11067394731465      1.54617925891532      5.43219505881525
  H   0.07447750912541      2.85798194957724      4.28875428011838
  C   2.51173758162267     -1.89100971258380     -0.15632736219293
  C   1.94612854749636      0.44931419161853     -1.12112069322850
  H   2.64722158089852     -2.24303706755986     -1.18020309908616
  H   1.97807106646307     -2.65141616754396      0.41793967911031
  H   3.50995573236818     -1.77334184650244      0.28954247753543
  H   -1.29617544312979      1.55127648260483     -1.85106574713161
  C   -0.08775606376184     -2.32117166844547     -2.10076567202684
  C   2.81495622471944      0.28638309825718     -2.21920199676398
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  C   2.95260251691072      1.29713608350641     -3.16396690819820
  C   1.36016431833338      2.65829939386483     -1.95705330475695
  C   2.22580792068508      2.48447490448444     -3.04249548700947
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  H   0.63312204928874     -3.05001681348082     -1.72271186683633
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  C   1.52357323622907     -2.25563846396358     -4.03890912690189
  C   1.99542310939641     -1.69907426525753     -5.22839927366758
  C   1.38846308537631     -0.55912623232576     -5.75580172196186
  C   0.30188803303164      0.01730016732734     -5.09425983345152
  H   -0.17187459755732      0.90759529428410     -5.49700372652737
  H   -1.02148376588637     -0.09659556373908     -3.40224611623670
  H   2.00287065718387     -3.13943258315814     -3.62494388835508
  H   2.84136982002619     -2.15241906485237     -5.73707003373211
  H   1.76237574017546     -0.11828963650971     -6.67525335201825
  H   2.74201093986644     -2.19077846219498      2.84278362187181
  H   0.61932568894785      3.10902789736269      1.66508301978024
  H   -5.54269706124222      0.17334271963024      1.81481375631519
  H   -2.05201048563208     -2.41460459121193      1.95202672248929
  H   -3.73136552019858      0.49923883482938     -2.34793218332389
  H   0.55247519158730      1.76922810979324     -0.16523988083229
  H   0.79092264683626      3.57859201203207     -1.85848880816073
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  H   3.62676523173754      1.15666380347150     -4.00310971503747
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FINAL SINGLE POINT ENERGY     -3683.220022744682
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UHF SPIN CONTAMINATION
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...
Expectation value of <S**2>     :     0.432997
Ideal value S*(S+1) for S=0.0   :     0.000000
Deviation                       :     0.432997
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References

1 (*a*) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka and F. Weigend, *WIREs Comput. Mol. Sci.*, 2014, **4**, 91–100; (*b*) TURBOMOLE V6.5 2013, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

2 F. Neese, *WIREs Comput. Mol. Sci.*, 2011, **2**, 73–78.

3 (*a*) K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283–290; (*b*) K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119–124; (*c*) R. Bauernschmitt, M. Häser, O. Treutler and R. Ahlrichs, *Chem. Phys. Lett.*, 1997, **264**, 573–578; (*d*) P. Deglmann, K. May, F. Furche and R. Ahlrichs, *Chem. Phys. Lett.*, 2004, **384**, 103–107; (*e*) C. K. Skylaris, L. Gagliardi, N. C. Handy, . G. Ioannou, S. Spencer and A. Willets, *J. Mol. Struct. (THEOCHEM)*, 2000, **501**, 229–239.

4 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **242**, 652–660.

5 (*a*) S. Grimme, A. Hansen, J. G. Brandenburg and C. Bannwarth, *Chem. Rev.*, 2016, **116**, 5105–5154; (*b*) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

6 (*a*) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465; (*b*) A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2005, **123**, 154101; (*c*) E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2005, **123**, 24101.

7 J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.

8 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

9 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.

10 A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799–805.

11 (*a*) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (*b*) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822; (*c*) J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406.

12 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.

13 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

14 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 5656-5667.

15 S. Grimme, *J. Chem. Phys.*, 2006, **124**, 034108.

16 For an excellent review, see: L. Goerigk and S. Grimme, *WIREs Comput. Mol. Sci.*, 2014, **4**, 576–600.

17 (*a*) F. Weigend, F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2003, **119**, 12753; (*b*) A. Hellweg, C. Hättig, S. Höfener and W. Klopper, *Theor. Chem. Acc.*, 2007, **117**, 587–597.

18 (*a*) S. Kozuch and J. M. L. Martin, *J. Comput. Chem.*, 2013, **34**, 2327–2344; (*b*) S. Kozuch and J. M. L. Martin, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20104–20107.

19 (*a*) A. Klamt, V. Jonas, T. Bürger and J. C. Lohrenz, *J. Phys. Chem. A*, 1998, **102**, 5074–5085; (*b*) A. Klamt, *J. Phys. Chem.*, 1995, **99**, 2224–2235.

20 (*a*) COSMOtherm, C3.0, release 1501, COSMOlogic GmbH & Co KG, http://www.cosmologic.de. (*b*) F. Eckert and A. Klamt, *AlChE J.*, 2002, **48**, 369–385.

21 (*a*) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829–5835; (*b*) K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119–124.

22 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479–483.

23 F. Weigend and M. Häser, *Theor. Chem. Acc.*, 1997, **97**, 331–340.

24 Basis sets, j-bases and c-bases: (*a*) D. H. Bross, J. G. Hill, H.-J. Werner and K. A. Peterson, *J. Chem. Phys.*, 2013, **139**, 094302; (*b*) K. E. Yousaf and K. A. Peterson, *Chem. Phys. Lett.*, 2009, **476**, 303–307; (*c*) N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2005, **123**, 064107; (*d*) C. Hättig, *Phys. Chem. Chem. Phys.*, 2005, **7**, 59–66; (*e*) F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 2002, **116**, 3175; (*f*) T. H. Dunning Jr., K. A. Peterson, and A. K. Wilson, *J. Chem. Phys.*, 2001, **114**, 9244; (*g*) R. A. Kendall, T. H. Dunning Jr. and R. J. Harrson, *J. Chem. Phys.*, 1992, **96**, 6796; (*h*) T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007.

25 C. Y. Legault, *CYLview*, 1.0b; Université de Sherbrooke, 2009. http://www.cylview.org (accessed 09.02.2018).

26 (*a*) *Avogadro: an open-source molecular builder and visualiyation tool. Version 1.2.0*. http://avogadro.cc (accessed 09.02.2018). (*b*) M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek and G. R. Hutchison, *J. Cheminformatics*, 2012, **4**, 17.

27 https://sites.google.com/site/orcainputlibrary/dft/double-hybrid-dft (accessed 09.02.2018).

28 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3093.

29 A. Ben-Naim and Y. Marcus, *J. Chem. Phys.*, 1984, **81**, 2016-2027.

30 C. B. Alcock, V. P. Itkin and M. K. Horrigan, *Can. Metall. Q.*, 1984, **23**, 309–313.

31 http://webbook.nist.gov/cgi/cbook.cgi?ID=C7440666

32 http://webbook.nist.gov/cgi/cbook.cgi?ID=C109999

33 S. Deb, B. A. Bayes, M. P. Minitti and P. M. Weber, *J. Phys. Chem. A*, 2011, **115**, 1804–1809.

34 (*a*) S. Yamanaka, T. Kawakami, H. Nagao and K. Yamaguchi, *Chem. Phys. Lett.*, 1994, **231**, 25–33; (*b*) K. Yamaguchi, F. Jensen, A. Dorigo and K. N. Houk, *Chem. Phys. Lett.*, 1988, **149**, 537–542.

35 (*a*) J. L. Sonnenberg and H. B. Schlegel, in *Computational Inorganic and Bioinorganic Chemistry,* (Eds: E. I. Solomon, R. A. Scott and R. B. King), John Wiley & Sons: Hoboken (USA), 2009; (*b*) J. M. Wittbrodt and H. B. Schlegel, *J. Chem. Phys.*, 1996, **105**, 6574–6577.
36 A. Gansäuer, *Chem. Commun.*, 1997, 457–458.
37 J. Streuff, M. Feurer, G. Frey, A. Steffani, S. Kacprzak, J. Weweler, L. H. Leijendekker, D. Kratzert and D. A. Plattner, *J. Am. Chem. Soc.*, 2015, **137**, 14396–14405.
38 *Origin* (OriginLab, Northampton, MA), http://www.originlab.com.
39 D. Jayatilaka and T. J. Lee, *J. Chem. Phys.*, 1993, **98**, 9734–9747.
40 T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem., Quant. Chem. Synp.*, 1989, **S23**, 199–207.
41 W. Jiang, N. J. DeYonker and A. K. Wilson, *J. Chem. Theory Comput.*, 2012, **8**, 460–468.
42 Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.